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"PHOTOCHEMICALLY INDUCED TRANSFORMATIONS OF TRANSITION METAL COMPLEXES"

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"PHOTOCHEMICALLY INDUCED TRANSFORMATIONS OF TRANSITION METAL COMPLEXES"

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Photolysis of the dinuclear complex $[(n^5\text{-}C_5H_5Fe(CO)_2]_2$ in $CHCl_3$ results in the formation of $(n^5\text{-}C_5H_5)Fe(CO)_2Cl$ through intermediate 17-electron radicals of the form $(n^5\text{-}C_5H_5)Fe(CO)_2$. The photolyses of the related diphosphine-bridged compounds $[(n^5\text{-}C_5H_5)Fe(CO)_2$-u-DPPX, where DPPX=DPPM, DPPE and DPPP and therefore are $(Ph_2P)_2CH_2$, $(Ph_2P)_2C_2H_4$ and $(Ph_2P)_2C_3H_6$ respectively, are described. The synthesis and photolysis of the analogous ruthenium DPPM dimer is also described. In contrast to the behavior of the simple iron dinuclear species, the DPPM and DPPE phosphine bridged compounds undergo photolysis in $CHCl_3$ to yield products containing formyl substitued cyclopentadienyl rings. Details of the reactions studied and product characterizations using multinuclear NMR, IR and single crystal X-ray diffraction techniques are described. A possible mechanism for the formation of the formyl derivatives is outlined. In the synthesis and purification of $[(n^5\text{-}C_5H_5)Ru(CO)]_2$-u-DPPM and the attempted synthesis of the $[(n^5\text{-}C_5H_5)Ru(CO)]_2$-u-DPPE, two ruthenium monomers of the form $(n^5\text{-}C_5H_5)Ru(Cl)DPPX$ resulted. A possible reaction pathway for the synthesis of these two monomers as byproducts in the ruthenium phosphine dimer preparation is suggested. Full structural and spectral characterizations of the monomeric compounds are included.

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Abstract

Photolysis of the dinuclear complex $[(n^5\text{-}C_5H_5)Fe(CO)_2]_2$ in $CHCl_3$ results in the formation of $(n^5\text{-}C_5H_5)Fe(CO)_2Cl$ through intermediate 17-electron radicals of the form $(n^5\text{-}C_5H_5)Fe(CO)_2$. The photolyses of the related diphosphine-bridged compounds $[(n^5\text{-}C_5H_5)Fe(CO)]_2$-u-DPPX, where DPPX = DPPM, DPPE and DPPP and therefore are $(Ph_2P)_2CH_2$, $(Ph_2P)_2C_2H_4$ and $(Ph_2P)_2C_3H_6$ respectively, are described. The synthesis and photolysis of the analogous ruthenium DPPM dimer is also described. In contrast to the behavior of the simple iron dinuclear species, the DPPM and DPPE phosphine bridged compounds undergo photolysis in $CHCl_3$ to yield products containing formyl substituted cyclopentadienyl rings. Details of the reactions studied and product characterization using multinuclear NMR, IR and single crystal X-ray diffraction techniques are described. A possible mechanism for the formation of the formyl derivatives is outlined. In the synthesis and purification of $[(n^5\text{-}C_5H_5)Ru(CO)]_2$-u-DPPM and the attempted synthesis of the $[(n^5\text{-}C_5H_5)Ru(CO)]_2$-u-DPPE, two ruthenium monomers of the form $(n^5\text{-}C_5H_5)Ru(Cl)$DPPX resulted. A possible reaction pathway for the synthesis of these two monomers as byproducts in the ruthenium phosphine dimer preparation is suggested. Full structural and spectral characterizations of the monomeric compounds are included.

Key Words: Photosynthesis, Organometallics, Reimer-Tiemann

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Background

Chemistry is the science that examines the structure, the properties and the physical and chemical changes of matter. Historically, chemistry as a discipline is a very young field with roots dating back to the 1800's when the first theories were proposed and confirmed by experiment.[1] Since that time the chemical community has grown from a small group of pioneers to a world-wide organization of scientists researching every aspect of the discipline.

During the evolution of chemistry, scientists became more specialized and began concentrating on well-defined areas of chemistry. Until recently, the field of chemistry was adequately subdivided into five major areas: analytical, biochemical, inorganic, organic and physical. In today's world these five areas are insufficient to describe the type of work that a particular chemist does since each subdiscipline encompasses a broad spectrum of ideas and concepts. To illustrate the diversity of each area the field of inorganic chemistry can be used.

While organic chemistry is the chemistry of compounds that focuses on carbon, inorganic chemistry can be broadly described as the chemistry of everything else. In a more formal sense, inorganic chemistry is defined as "the study of the structures, the properties, reactivities, and interrelationships of the chemical elements and their compounds."[2] The first subdivision in inorganic chemistry is

between nonmetals and metals. Metal chemistry can be further broken down into the chemistry of the transition metals, the post-transition metals and the inner-transition metals (Table 1). Each of these metal types are important in the fields of bioinorganic, classical coordination and organometallic chemistry (Figure 1).

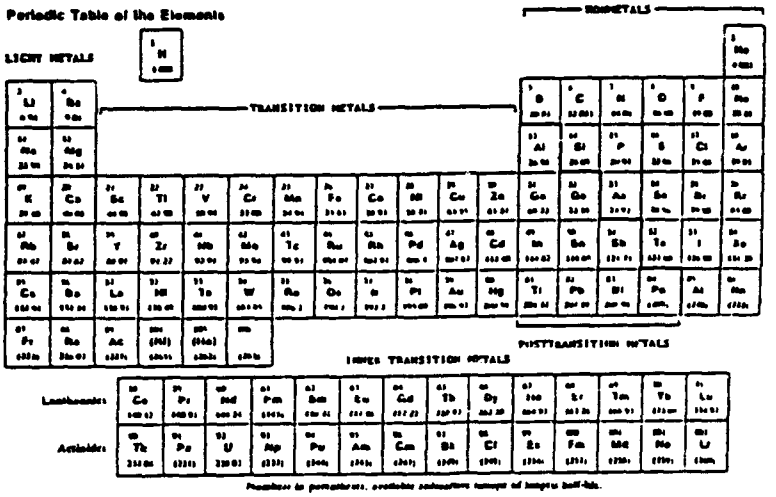


Table 1: The Periodic Table of the Elements

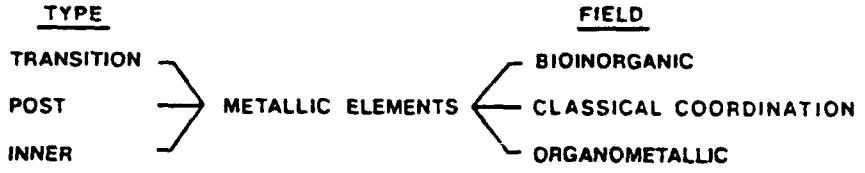


Figure 1: Types and Fields of Metallic Elements

Bioinorganic compounds are important in living systems and include such complexes as hemoglobin and Vitamin B-12 (Figure 2).[3] Hemoglobin is the biomolecule in the blood of higher mammals and humans that is responsible for oxygen transfer from the lungs to the muscles. At the center of the molecule is an iron atom which is encapsulated in a porphyrin ring. Vitamin B-12 is a cobalt-containing coenzyme that is essential for the production of red blood cells.

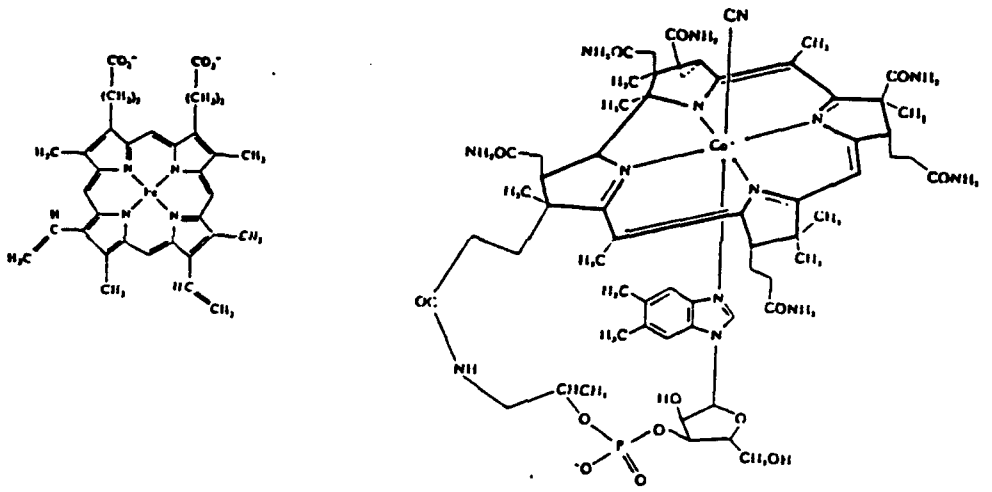
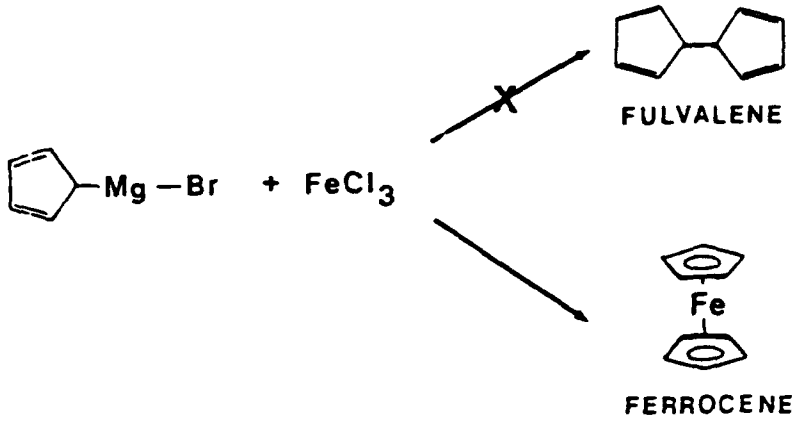


Figure 2: The Heme group (left) and Vitamin B-12

Classical coordination compounds contain a metal center which is bonded to nonmetal substituents referred to as ligands. $Na_2[NiBr_4]$ is a classical coordination compound with four bromine ions attached to the nickel center. The Na^+ cations act to counterbalance the charge of the tetrabromo nickel anion.

The third type of metal compounds, organometallics, has shown significant development during the last forty years and is similar in structure to classical coordination compounds. Organometallic compounds contain a metal center in a low valence state (+1,0,-1) that is bonded to either neutral or negatively charged atomic or molecular fragments (CO, $P(C_6H_5)_3$, Cl^-) which act as ligands. What makes organometallics different from classical coordination compounds is that at least one of the bonds in the compound must be a metal-carbon bond. This M-C bonding arrangement has allowed the synthesis of new and exciting compounds that had previously never been thought possible.

Even though the synthesis of the first organometallic compound can be traced back to 1827 with the synthesis of Zeise's salt[4], $K[Pt(C_2H_4)Cl_3]$, the field did not become a specialized area of study until 1951. In that year, Kealy and Pauson attempted to synthesize fulvalene by reacting the Grignard reagent cyclo-C_5H_5MgBr with $FeCl_3$ in anhydrous diethyl ether (Scheme 1).[5] Instead of synthesizing fulvalene, the isolated product contained an iron atom "sandwiched" between two parallel cyclopentadienyl rings. This air-stable orange solid was determined to have the formula $(\eta^5\text{-}C_5H_5)_2Fe$ and is commonly referred to as "ferrocene." This discovery led to the synthesis of other sandwich metallocenes with metal atoms bonded to cyclopentadienyl rings as well as other types of cyclic organic ligands (Figure 3).[6] Shortly after the



Scheme 1: Synthesis of Ferrocene

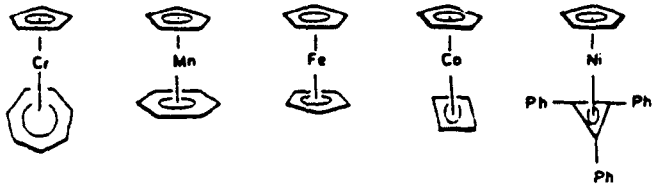
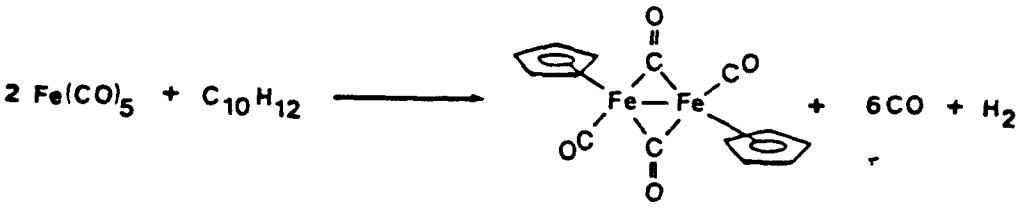


Figure 3: Various types of metallocenes

discovery of ferrocene, compounds containing various other types of organic ligands were synthesized. In 1955, Wilkinson, Cotton and Piper[7] reported the synthesis of a carbonyl (CO) cyclopentadienyl dimer through the reaction of $Fe(CO)_5$ with $C_{10}H_{12}$ (Scheme 2). This compound became the focal point for the synthesis of a wide variety of substituted iron dimers as well as monomeric metal complexes.

To synthesize organometallic compounds, a variety of experimental procedures are available, but the most commonly



Scheme 2: Synthesis of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$

used are thermolysis, the addition of heat, and photolysis, the irradiation with light. Thermolysis is based upon the principle of temperature-energy correlation: as temperature increases, energy increases. Thus a reaction that needs a substantial amount of energy to proceed could be carried out at increased temperatures. A disadvantage to a thermolysis technique is a lack of selectivity. Since the molecule as a whole undergoes an increase in energy, there is limited control in a thermolysis reaction of which bonds are broken and which are maintained.

Photolysis is an alternative technique that allows a selective amount of energy to be added to the reactants. By controlling the wavelength of the photolysis lamp source, the experimenter may selectively excite molecules to their optimum reactive state. Because the energy content of the photons of light depends upon the frequency, the correct photolysis lamp source must be selected in order for the reaction to be successful.[8]

After the synthesis and purification of an organometallic compound has been completed, the final step is identification of any and all products. During the first half of the twentieth century chemical analysis consisted of reacting an obtained product with known reagents to see if a precipitate formed or a color change occurred. Modern science has been able to minimize qualitative and quantitative "wet chemistry" characterization techniques as a result of the rapid development of a vast array of highly sensitive and accurate analytical instruments. Today's instruments are able to analyze milligrams of sample with accuracies in the parts per billion range. Because of the advancements in the development and improvement of instrumental technologies, scientists are now able to analyze reaction products more easily, quickly and with greater accuracy and precision. Instrumental techniques are available to identify numbers and types of functional groups present in a compound as well as the exact structural composition of the molecule.

One of the most useful instruments that an inorganic chemist has available, and one of the most popular for initial characterization of a product, is an Infrared (IR) spectrometer which scans the range from 4000 cm^{-1} to 670 cm^{-1} in the electromagnetic spectrum. IR energy is not sufficient to break molecular bonds, but it does excite various rotational and vibrational transitions of atoms in a molecule. Atoms are held together in a molecule by bonds that do not have a static

distance. The movement of a particular pair of bonded atoms occurs at a defined frequency. When energy of this frequency is added to the molecule, the amplitude of oscillation of the bonded atoms increases. Using this principle, an infrared spectrometer irradiates a sample over a range of frequencies and then monitors the amount of energy absorbed by the sample. If there is a bond within the sample which oscillates at a frequency within the infrared region, the instrument will record the energy absorption as a band in the spectrum plot.[9]

From the absorption bands, the scientist can determine the types of functional groups within the compound by using known bond-frequency tables. Examples are N-H stretches which always absorb near 3500 cm^{-1} and C-H stretches which occur near 3000 cm^{-1}. In addition, multiple functional groups in a compound may have a simple IR spectrum due to the symmetry of the molecule. For example, $Mo(CO)_6$ has only one band because all six of the carbonyl ligands have coincident absorptions. In some compounds, symmetrical and asymmetrical stretching bands are evident in the IR spectrum when identical, nonsymmetrical functional groups are present (Figure 4).[10]

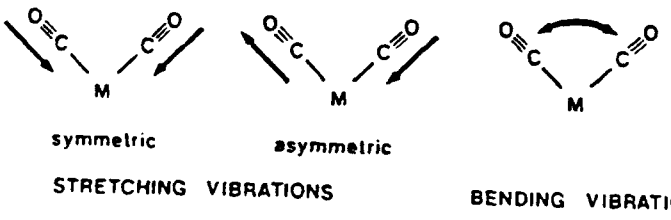


Figure 4: Various vibrations which can be observed by Infrared Spectroscopy

Using this information and applying it to organometallic compounds, one can analyze the ligands that are bonded to the metal center. Organometallic compounds frequently contain carbonyl ligands whose absorption bands are in the 1700-1860 cm^{-1} region if they are bridging (C=O) and 1850-2125 cm^{-1} region if they are terminal (C O).[11] Therefore, the location, presence or absence of carbonyl bands in the IR can be used to determine if the desired products of a reaction have been synthesized. IR can also show other stretching or bending vibrations which indicate the presence of other ligands in the organometallic compound. Two examples would be M-X absorption bands in the 300 cm^{-1} range, while M-P stretching frequencies vary between 170-460 cm^{-1} as a function of metal identity.[12] This functional group and bonding information is extremely useful in indicating what types of ligands are present in the synthesized compounds.

In addition to Infrared spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy can also be used to determine the types of functional groups present in a sample; however, NMR can reveal even more information about a compound. NMR spectroscopy not only generates peaks in regions characteristic to certain functional groups, it also allows detection of magnetic relationships between atoms within a molecule and, ultimately, determination of molecular structure.[13]

A nucleus of an atom has a spin which can be interpreted

as the rotation of the nucleus about an axis. Along with spin, an atom's nucleus also has a charge. A spinning charged nucleus produces both an electrical and magnetic field analogous to the fields produced from a current traveling through a coil of wire. Thus, this spinning charge produces a magnetic moment which is orientated along the spin axis of the atom. When a nucleus is placed within an exterior magnetic field, the magnetic moment of the nucleus orientates itself with or against the field. If the spin is aligned with the exterior field, the nucleus is in a low (relaxed or ground) energy state. If the spin is against the exterior field, the nucleus is in a high energy state. When energy of the proper frequency is added to the atom, the spin of the nucleus will go from a low to a high, or excited, energy state.

In today's modern NMR instruments, the addition of energy to excite the nuclei of atoms is done by pulsing the sample with broad band energy so that all of the nuclei simultaneously become excited. Following the pulse, the molecule undergoes a relaxation phase which allows the nuclei to return to their ground states and release the energy they absorbed (Figure 5)[14]. The frequencies of energy released are monitored by the instrument and the process is repeated as many times as desired. A multiple-step analysis is done so that the signal-to-noise ratio is improved. This improvement is a result of the additive nature of the positive signal

while random zero-mean electronic noise is averaged out. Following the data acquisition, the information is processed using a Fourier transformation.

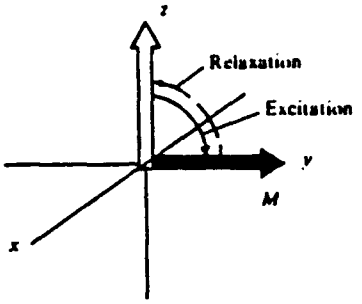


Figure 5: The excitation and relaxation states of nuclei during NMR analysis.

After the data is processed, it is plotted as various peaks with the spectrum axis calibrated in parts per million (ppm). To understand how data is plotted and interpreted, an example of the ^1H NMR spectrum of iodoethane (Figure 6) will be analyzed. Iodoethane, CH_3CH_2I, has two different "types" of hydrogen groups in the molecule: the methyl ($-CH_3$) hydrogens and the methylene ($-CH_2-$) hydrogens. On the spectrum, these magnetically nonequivalent hydrogens are represented by a quartet at 3.19 ppm for the methylene hydrogens and by a triplet at 1.84 ppm for the methyl hydrogens. Electronegative atoms, such as chlorine, iodine or oxygen, deshield the hydrogen nuclei because they absorb some of the electron density from the surrounding hydrogens and leave them with an electron shell which is not as dense as usual. Aromatic substituents, such as cyclopentadienyl or phenyl rings, also

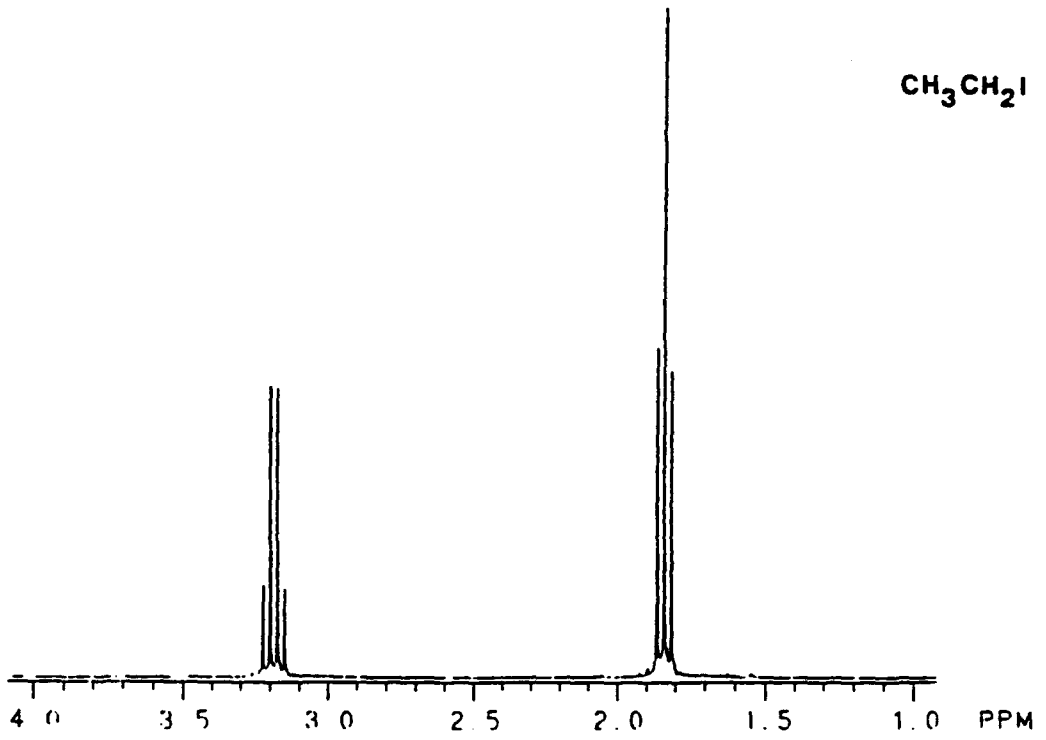


Figure 6: ^1H NMR Spectrum of Iodoethane.

deshield hydrogen atoms causing the peaks to be further to the left on the spectrum plot. Thus, each chemically distinct nucleus or group of nuclei will have a unique peak location or chemical shift in the NMR spectrum as a result of the chemical composition and symmetry properties of the molecule.

In addition to the chemical shift information about a particular nucleus or group of nuclei, the ^1H NMR spectrum also contains coupling constant information. There are mutual interactions between spinning nuclei in a molecule which result in coupling. Therefore, in the NMR spectrum, each type

of nucleus that undergoes coupling will appear as a multiplet instead of as a singlet resonance. In the example of iodoethane, coupling exists between the methylene hydrogens and the methyl hydrogens. The two methylene hydrogens can have four possible combinations of spin states, all of which have equal probability of occurring. If each spin is represented by an arrow, then the four possible spin states are as shown in Figure 7.[15] One combination has the spin states parallel to the external magnetic field, B_o, and another combination has the spin states anti-parallel to the field. There are also two combinations in which the spins are opposed to each other. Collectively, these combinations are represented by a triplet in the NMR spectrum with relative peak intensities of 1:2:1 due to the population ratios of the spin states. The separations between the lines of the triplet are equal to the coupling constant, J, in Hertz.

In an analogous fashion, the possible spin states for the methyl hydrogens can be derived and are also shown in Figure 7. Again, there is one case with spins aligned with the external field and a second pattern with spins opposed to the field. Since the methyl has three hydrogens, there is a greater variation in the intermediate spin combinations as shown. These patterns would be represented as a quartet in the NMR spectrum with relative peak intensities of 1:3:3:1. Inspection of these two multiplets for the methyl and methylene hydrogens indicate a simple relationship for

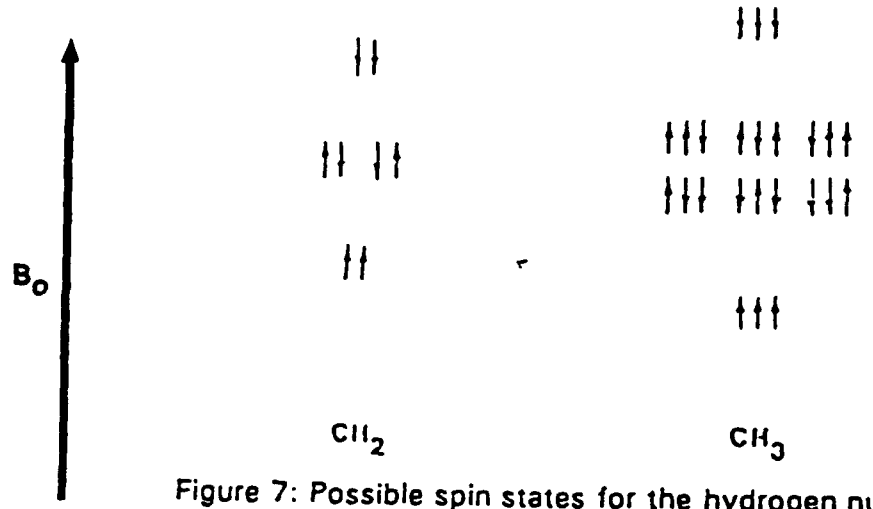


Figure 7: Possible spin states for the hydrogen nuclei of iodoethane

predicting the number of peaks in a spectrum. For a particular group of magnetically equivalent hydrogens, the splitting pattern can be predicted by looking at the number of hydrogens on the adjacent atom and adding one.

Coupling in a ^{1}H NMR spectrum is not restricted to the interactions between hydrogens. Many other types of NMR active nuclei will cause coupling, with the most common of these being ^{13}C, ^{31}P and ^{19}F. Unless specifically decoupled during the NMR experiment, these nuclei will exhibit secondary coupling with the hydrogen nuclei in the molecule. Simple doublets, triplets and quartets become complex multiplets as a result of this additional heteronuclear coupling. Together the chemical shift and coupling information make it possible to determine the numbers of unique spinning nuclei present in a compound as well as the bonding arrangements of the substituents.

Two forms of spectroscopy have been discussed and together they provide a wealth of information to the chemist. Even though IR and NMR are very powerful analytical tools, it is sometimes necessary to use additional techniques to confirm the structure of a compound. One such technique is mass spectroscopy (MS). A mass spectrometer is an instrument in which ions are produced from a sample, separated according to their mass-to-charge ratios, and then recorded, in terms of intensity.[16]

When a sample is injected into a mass spectrometer, the compound is converted to a vapor, ionized and subsequently analyzed. The ions are first accelerated by application of a potential of several thousand volts per meter and then sequentially passed through electrostatic and magnetic analyzers. Electrostatic or magnetic fields perpendicular to the motions of the ions are applied. The net effect is that the ions are focused in a circular path where the radii is dependent upon the mass-to-charge ratio of the ions. Variation of the magnetic field brings the ions into the detector as a function of their masses and the ion current is measured. A mass spectrum is plotted in the form of ion current versus mass-to-charge ratio.

The simplest process that occurs in a mass spectrometer involves the interaction of an electron with a molecule. This results in the loss of an electron from the compound and the formation of a radical cation. This ion, which has

effectively the same mass as the parent compound, is called the molecular ion. Usually it is the ion with the highest mass in the spectrum. It is therefore often possible to determine the molar mass of a compound by simply looking for the highest mass peak in its mass spectrum. Further fragmentation of the molecule can occur, so that the spectrum which is recorded contains peaks for many ions. The abundances of these ions depend upon their stabilities or lifetimes and the stabilities of their precursors. It is possible to determine the stepwise breakdown of a compound into its functional groups through a careful analysis of a mass spectrum.

The three techniques that were previously described are routinely used by chemists. From the IR, NMR and MS analysis, the structure of a compound can be determined by piecing together information about the functional groups and fragments in the molecule. However, a definitive characterization of the structure may not be possible solely on the basis of IR, NMR and MS data. In this case, single crystal X-ray diffraction can be the most useful experiment since this technique gives the exact molecular structure of a substance. The results of an X-ray structure solution are atom positions, bond distances and bond angles within a molecule. Therefore, X-ray structure solution is a full molecular structure characterization.[17]

The first step in understanding what happens during X-ray

analysis is to examine the process of crystallization. When molecules crystallize, they do so in a repeating pattern resulting in a regular array of molecules. This array is called the crystal lattice and is the basis for X-ray diffraction. When a crystal is subjected to a beam of X-rays, diffraction occurs and can be described as the X-rays being "reflected" from the planes in the crystal lattice. In the X-ray experiment, reflections are collected as a function of the orientation of the crystal planes relative to the direct X-ray beam. The intensity of each reflection depends upon the nature and location of each atom in the unit cell, which is the smallest volume element from which the entire crystal can be reproduced through only x, y and z translations.

From the intensities of the reflections that result from the experiment, the structure solution can be obtained. The initial step in this process is the conversion of the experimental intensities into structure factors. It is ultimately the structure factors which are needed to determine the structure of the crystal. Intensities are a scalar result of the X-ray experiment and have only a magnitude. Structure factors have vector properties and have a magnitude and a phase. Since only intensities can be measured, the experimental data contains no phase information. This is the classical phase problem of crystallography. Structure solution is the determination, by mathematical techniques, of the proper phases of the structure factors.

There are two common methods for structure solution. The first method, the Patterson function, applies a Fourier transform to the magnitudes of the structure factors only. This function results in vectors corresponding to inter-atomic positions within the crystal. The vectors are weighted according to the product of the atomic numbers of the atoms which they connect. Therefore, the largest peaks in the Patterson list are typically the vectors between the heaviest atoms in the crystal. This method of structure solution is particularly useful for a molecule containing heavy atoms, such as iron and ruthenium.

A second common technique used for structure determination is Direct Methods. This technique takes advantage of statistical relationships which exist between the experimental intensities. Application of this method then produces a number of solutions which are ranked in terms of their probability of correctness. The crystallographer searches for a highly probable solution which is consistent with the chemistry of the compound.

After a partial solution has been obtained, the standard crystallographic model is applied. This model places spherical neutral atoms at x, y and z positions in the unit cell and associates an isotropic thermal motion with each atom. The electron density at these atom positions is then used to generate a set of "calculated" structure factors. Calculated and experimental structure factors are then

compared in a least squares refinement process which allows the atom positions and thermal parameters to change in order to achieve a best fit. Missing atoms are then located using a Fourier transform of the difference between experimental and calculated structure factors using the calculated phases. This is called the difference Fourier technique. Once all the atoms in the structure are located, the atomic positions are further refined with anisotropic thermal motion until the best agreement between experimental and calculated structure factors is obtained. This final agreement is known as the R factor which is defined[18] as:

$$R = \text{sum}||F_o| - |F_c||/\text{sum}|F_o|$$

Typical values of R factors are in the range of two to seven percent.

Through X-ray crystallography, IR, NMR and MS, the chemist can ascertain the structure of almost any compound.

Introduction

Photolytic investigations of metal-metal bonded compounds have become an area of increased interest, with carbonyl bridged compounds receiving an abundance of attention due to the variety of reaction possibilities. Primary reaction pathways include: metal-metal bond homolysis, conversion of bridging carbonyl ligands to terminal species and/or carbonyl ligand dissociation. In homolysis, the metal-metal bond is cleaved which results in two very reactive metal radical species in solution. When the bridging carbonyls are affected, they can either become terminally bound or they can be completely dissociated from the dimer as carbon monoxide.

Numerous research groups have explored the chemistry of bimetallic systems while maintaining the dimeric character of their compounds. In one study Bitterwolf, et al.[19], studied coupled ring dimer systems containing ruthenium under photolytic conditions. It was determined that in the presence of a halide donor ($CHCl_3$ or CCl_4) the metal-metal bond breaks, the bridging carbonyls become terminal and the halide group (X) is included in the final product. When RX is not present, photolysis of the ruthenium compounds forms "twist" compounds in which one ruthenium bridges two cyclopentadienyl groups and the other ruthenium is only bonded to one of the cyclopentadienyl groups. (Figure 8)

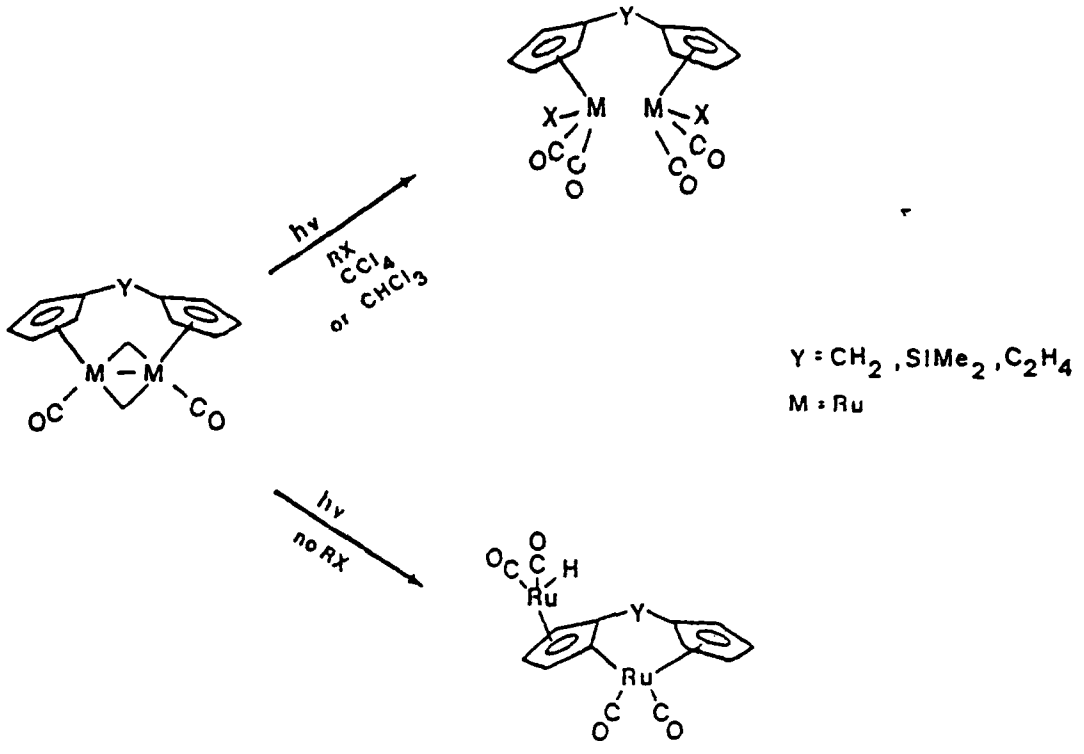


Figure 8: Coupled Ring Dimers of Ruthenium

The purpose of this Trident research project was to investigate metal dimer systems in which the metal atoms were linked via a bridging bidentate phosphine ligand. It was expected that under photolytic conditions any bridging carbonyls would become terminal and the metal-metal bond would cleave to form a single compound containing two metal radicals. Subsequent photolysis of the reactive radical species in an alkyl halide would be expected to yield a bidentate phosphine dimer containing terminal carbonyls and two chloro ligands. (Figure 9)

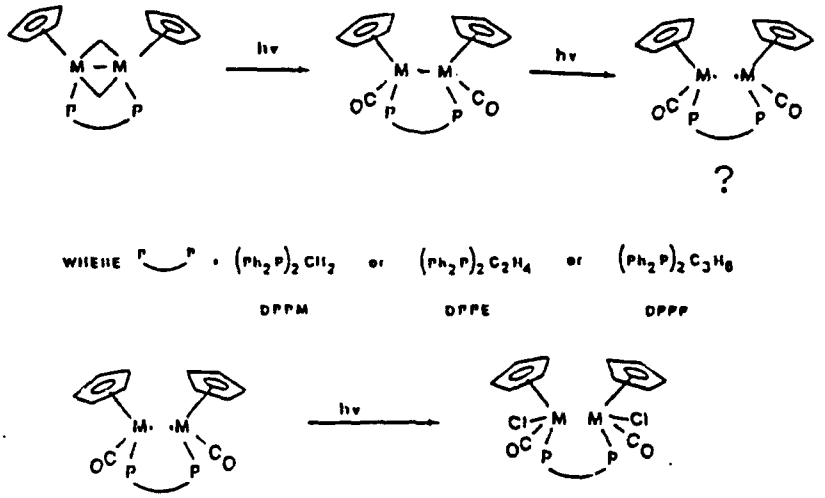


Figure 9: Expected Reaction Pathway Via Photolysis for Iron and Ruthenium Dimers

In order to test this hypothesis, the photolysis of $(n^5\text{-}C_5H_5)_2Fe_2(u\text{-}CO)_2(u\text{-}DPPM)$, $(n^5\text{-}C_5H_5)_2Fe_2(u\text{-}CO)_2(u\text{-}DPPE)$, $(n^5\text{-}C_5H_5)_2Fe_2(u\text{-}CO)_2(u\text{-}DPPP)$ and $(n^5\text{-}C_5H_5)_2Ru_2(u\text{-}CO)_2(u\text{-}DPPM)$, in chloroform was examined, where DPPM = bis(diphenylphosphino)methane, DPPE = 1,2-bis(diphenylphosphino)ethane and DPPP = 1,3-bis(diphenylphosphino)propane. It was anticipated that the $CHCl_3$ would be an efficient scavenger for any metal-metal bond homolysis product that had an extended lifetime. It was discovered that the FeDPPP dimer reaction proceeded by metal-metal bond homolysis while photolysis of the other three dimeric compounds resulted in totally unexpected, and previously unobserved, metal-metal bonded complexes.[20]

Results and Discussion

$(n^5\text{-}C_5H_5)_2Fe_2(u\text{-}CO)_2(u\text{-}DPPX)$

The compounds $(n^5\text{-}C_5H_5)_2Fe_2(u\text{-}CO)_2(u\text{-}DPPX)$, where X = methyl (I), ethyl (II), and propyl (III), were prepared according to published procedures.[21] (Figure 10) When compounds I and II were photolyzed, the green solution became brown. After the solvent was removed through vacuum evaporation, the resultant oil was chromatographed on Grade III (6% water by weight) alumina. Petroleum ether/ chloroform were the eluting solvents and in both cases a golden brown band was recovered from the column which yielded a brown solid upon removal of the solvent or through crystallization.

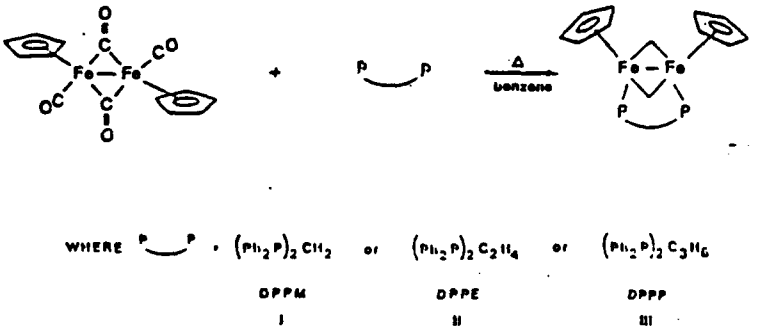
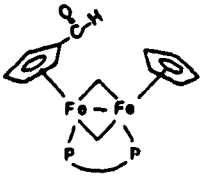


Figure 10: Synthetic Pathway for Compounds I, II and III

Compounds IV and V (X = methyl and ethyl) are the products isolated from the photolysis reactions of I and II, respectively. (Figure 11) The analysis of room temperature ^1H and ^{13}C NMR spectra clearly indicated that one of the two cyclopentadienyl rings had been substituted. Characteristic resonances in both the carbon and hydrogen spectra and the



WHERE $\overset{P}{\frown}\overset{P}{}$ = $(Ph_2P)_2CH_2$ or $(Ph_2P)_2C_2H_4$

DPPM DPPE

IV V

Figure 11: Isolated Formyl Products from the Photolysis Reactions of FeDPPM and FeDPPE Dimers

appearance of two new bands (1658 cm^{-1} and 1655 cm^{-1}, respectively) in the IR spectra suggested the presence of a formyl group in the molecule. Further, the IR spectra showed little change in the CO stretches from the starting materials. The bridging carbonyl resonances of the compounds described in this paper were not located in the ^{13}C NMR spectra. This result is not unexpected since the carbons of the carbonyl ligands are coupled to the phosphorous atoms and are bonded to an electronegative atom, oxygen. The ^{31}P NMR of spectrum of **IV** consisted of a clean AB pattern centered at 84.48 and 81.47 ppm. This pattern is downfield of the singlet resonance of **I** which is at 86.63 ppm. The ^{31}P of **V** was found to have two singlets at 68.52 and 64.11 ppm, slightly downfield from the singlet resonance of **II** at 69.76 ppm. Mass spectrometry of **IV** and **V** revealed a parent mass fragmentation pattern consistent with a formyl derivative of **I** and **II**, respectively. The final

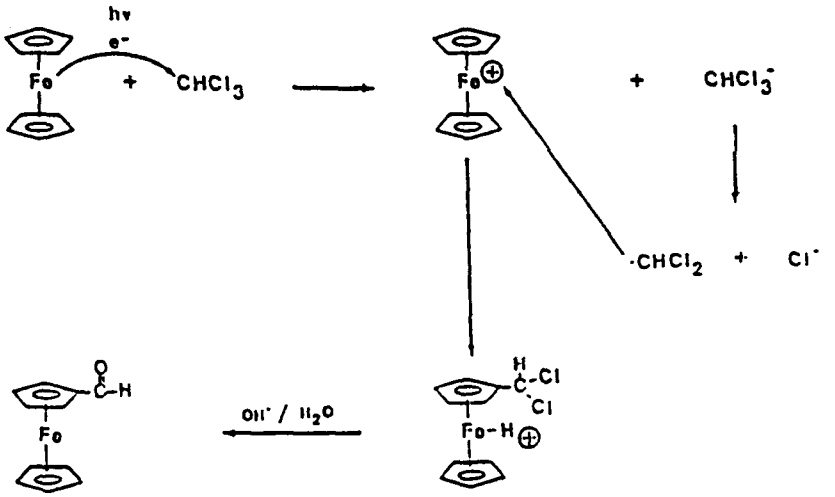
structures of IV and V were confirmed using X-ray crystallography and the results are described in this paper.

When compound III was photolyzed a similar color change from green to brown resulted, but a more polar solvent mixture (dichloromethane/methanol) was required for the removal of the product, VI, off the chromatography column. The brown solid, which is unstable upon storage, has a single carbonyl stretching band at 1967 cm^{-1} which is consistent with a terminal carbonyl. There is an absence of stretches in the 1700-1860 cm^{-1} region which could be associated with bridging carbonyls or formyl groups. The observed stretch is similar to that of $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)Cl$ which was reported to be 1963 cm^{-1} in Nujol.[22] These findings suggest that photolysis of compound III involves a homolysis of the iron-iron bond followed by reaction of the iron radicals with the chlorinated solvent.

To insure that the bridging carbonyls on the starting materials were not opening during the photolysis, compound I was photolyzed in Nujol at 77K and monitored using infrared spectroscopy. No change occurred in the IR spectrum after an hour. Compound I was also photolyzed in benzene and, except for slight decomposition, no isolatable product resulted.

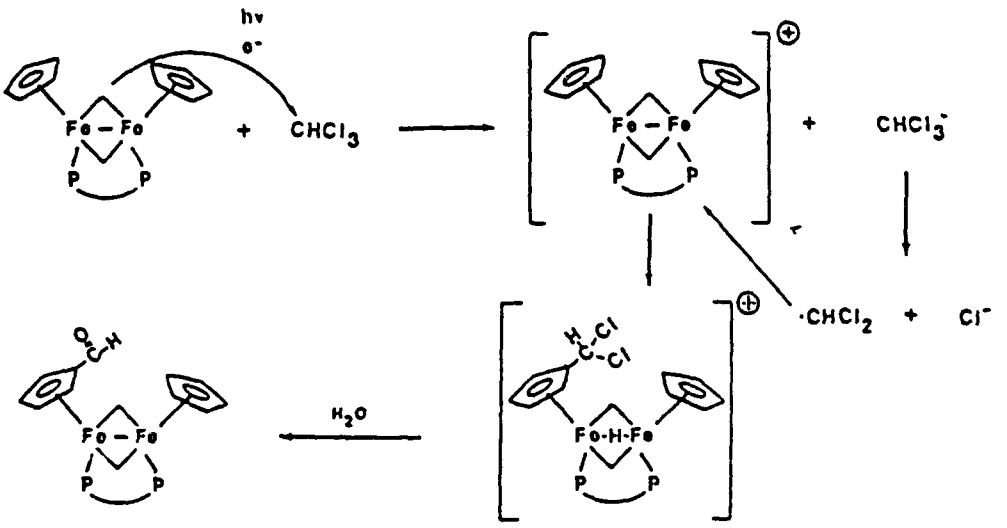
The reactions of I and II are similar to the work of Sugimori and coworkers on the photochemical reaction of ferrocene in halocarbon solvents in which compounds containing formyl, carboxylic acids and esters were isolated.[23] Hirao and

coworkers also reported similar studies involving electron-rich arene compounds.[24] These authors suggested that a photochemical Reimer-Tiemann reaction induced an electron transfer from the ferrocene to the $CHCl_3$ (Scheme 3). This transfer resulted in a ferrocinium ion, a chloride ion, and a $CHCl_2$ radical. An exo attack of the $CHCl_2$ radical on a cyclopentadienyl ring of the 17-e^{-1} ferrocinium ion yields a protonated ferrocene intermediate. The formyl derivative is then produced upon work-up following deprotonation and hydrolysis of this intermediate.



Scheme 3: Proposed Mechanism for Ferrocene System

It is proposed that formation of compounds IV and V are a result of a similar mechanism (Scheme 4). When compounds I and II are photolyzed, an electron transfer from the metal dimer to the solvent occurs. Subsequent radical attack occurs to form a protonated intermediate containing a bridging



Scheme 4: Proposed Mechanism for Bimetallic System

hydride between the two iron atoms of the dimer. Hydrolysis occurs during work-up and the isolated product is the formyl derivative. Because of the previous studies done by Furguson and coworkers[25] which showed that compounds I and II can be oxidized to the corresponding stable monocations, the generation of the monocations of I and II by photochemical charge transfer is reasonable under the reaction conditions described.

Photolysis of I was also carried out in an NMR tube at room temperature and analyzed at various intervals using an NMR spectrometer. During the reaction, severe decomposition occurred but the presence of a singlet at approximately -5 ppm in the proton spectra indicates the presence of a metal hydride. This supports the theory of a bridging metal hydride intermediate in the mechanism.

Differences in the behavior of compounds I, II and III can be explained by the steric strain imposed on the metal-metal bond by the seven-membered ring [Fe_2DPPP] in the DPPP compound. The DPPM and DPPE ligands would be expected to stabilize the metal atoms to homolysis while the strain in the DPPP derivative would be relieved by breaking the iron-iron bond. That steric strain is responsible for governing the reaction pathways for compounds I, II and III is further supported by the infrared spectra of these compounds. The IR spectra of reaction mixtures of I and II show only bridging carbonyl bands while the reaction mixture of III shows only a terminal carbonyl band.

X-ray structures for compounds I (Figure 12), II (Figure 13), IV (Figure 14) and V (Figure 15) were completed. Selected bond lengths for the four compounds appear in Table 2. The solid state structure of II contains a racemic mixture resulting from both enantiomers of the compound. The structures of compounds I and IV and compounds II and V are effectively superimposable except for the presence of the formyl group. The metal-metal bond lengths of 2.519(6) angstroms for I, 2.516(2) and 2.512(1) angstroms for the two independent molecules of II, 2.526(1) for IV and 2.527(1) angstroms for V compare favorably with the value of 2.532(2) angstroms reported by Wright, et all., for $Me_2Si(\eta^5\text{-}C_5H_4)_2\text{-}Fe_2\text{-}(u\text{-}CO)_2(u\text{-}DPPE)$.[26] All of the iron-iron bond lengths are slightly shorter than the 2.534(2) angstrom Fe-Fe distance in

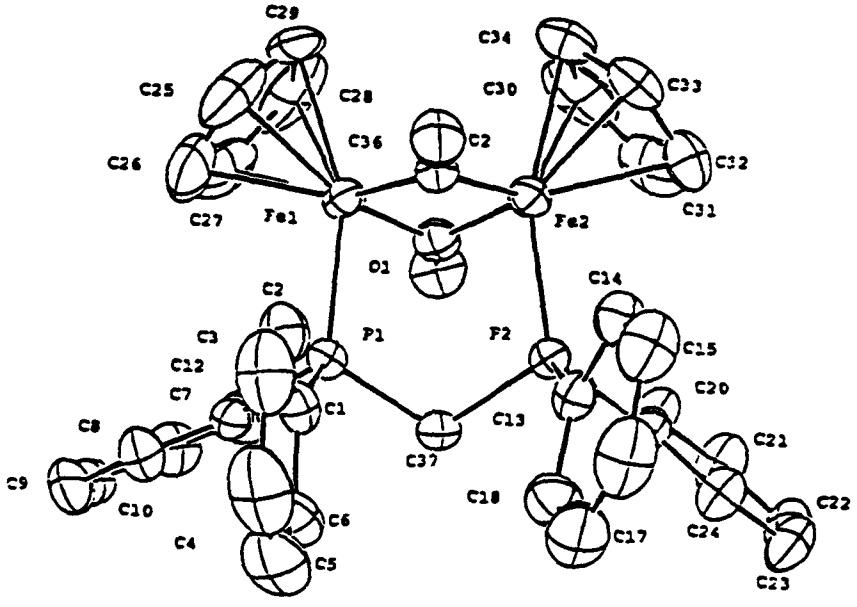


Figure 12: ORTEP of Compound I

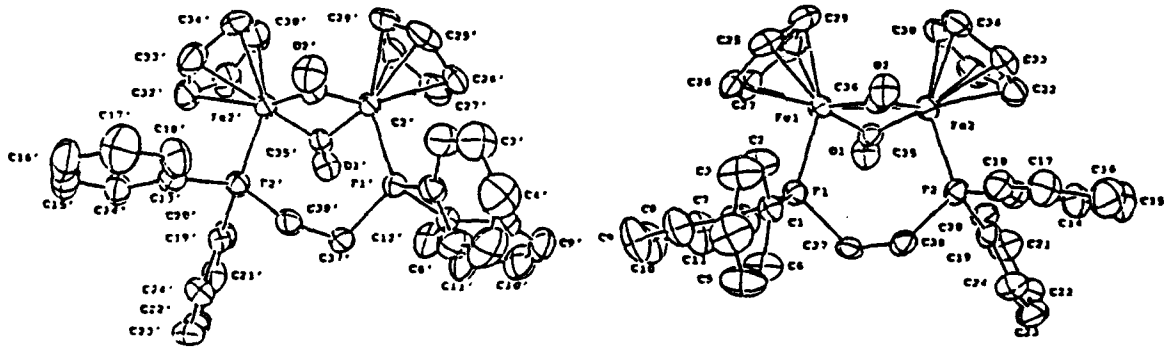


Figure 13: ORTEPs of Compound II

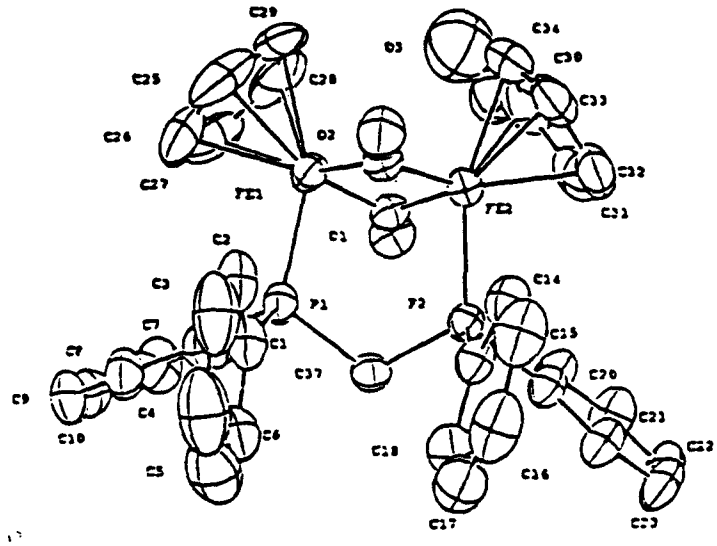


Figure 14: ORTEP of Compound IV

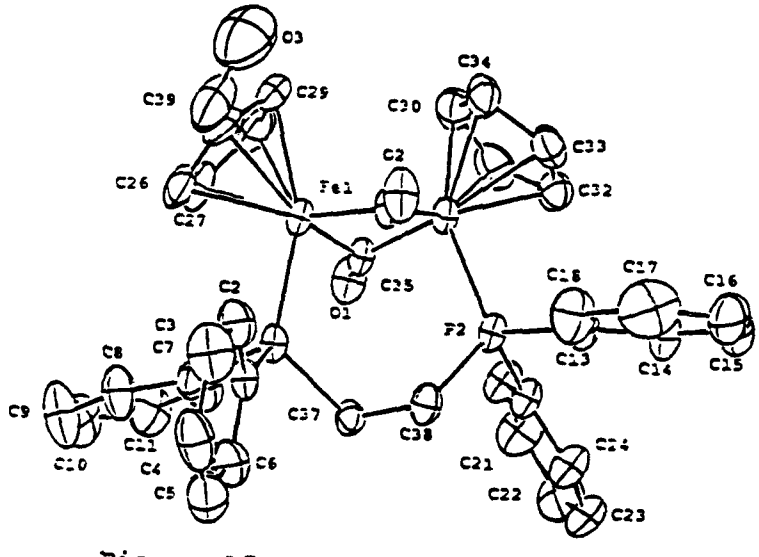


Figure 15: ORTEP of Compound V

Bond Type	Bond Lengths in Angstoms				
	I	II		IV	V
		a	b		
Fe1 - Fe2	2.519(6)	2.516(1)	2.512(1)	2.526(1)	2.527(1)
Fe1 - P1	2.176(7)	2.172(2)	2.182(2)	2.182(1)	2.197(2)
Fe2 - P2	2.191(7)	2.180(2)	2.177(2)	2.192(1)	2.188(2)
Fe1 - C35	1.903(2)	1.922(4)	1.918(8)	1.910(4)	1.926(7)
Fe1 - C36	1.909(3)	1.884(8)	1.906(7)	1.910(5)	1.916(8)
Fe2 - C35	1.900(3)	1.908(8)	1.887(6)	1.906(5)	1.904(8)
Fe2 - C36	1.906(2)	1.902(6)	1.913(8)	1.891(4)	1.917(7)

Table 2: Selected Bond Lengths for Compounds I, II, IV and V

$[(n^5\text{-}C_5H_5)Fe(CO)_2]_2$.[27] The shorter metal-metal bond lengths in compounds I, II, IV and V are most likely due to the presence of the bridging phosphine ligand.

$(n^5\text{-}C_5H_5)_2Ru_2(u\text{-}CO)_2(u\text{-}DPPX)$

In order to synthesize the ruthenium phosphine-bridged dimer, two different methods were attempted. The cyclopentadienyl-tetracarbonyl starting material, $(n^5\text{-}C_5H_5)_2Ru_2(CO)_4$ was prepared according to published methods.[28] In an analogous fashion to the iron synthesis, $(n^5\text{-}C_5H_5)_2Ru_2(CO)_4$ was refluxed with a quantitative amount of DPPM in benzene under a nitrogen atmosphere. The reaction proved to be unsuccessful and was repeated in refluxing xylenes at 139-141°C. While a small amount of the desired $(n^5\text{-}C_5H_5)_2Ru_2(u\text{-}CO)_2(u\text{-}DPPM)$ product was

obtained, isolation of the phosphine dimer out of the xylene solvent was difficult. It therefore became necessary to develop an alternative synthetic route to obtain the necessary compound. The successful synthesis was the photolysis of the reactants in benzene for eight to ten hours under a steady stream of nitrogen. The solution changed color from golden-yellow to red during the course of the reaction. After removal of the solvent, the resulting oil was chromatographed on Grade III alumina using petroleum ether/benzene as the eluting solvents. The product, compound VII, was orange-yellow in color and was obtained in a very low yield. The final structure of VII was confirmed using X-ray crystallography (Figure 16).

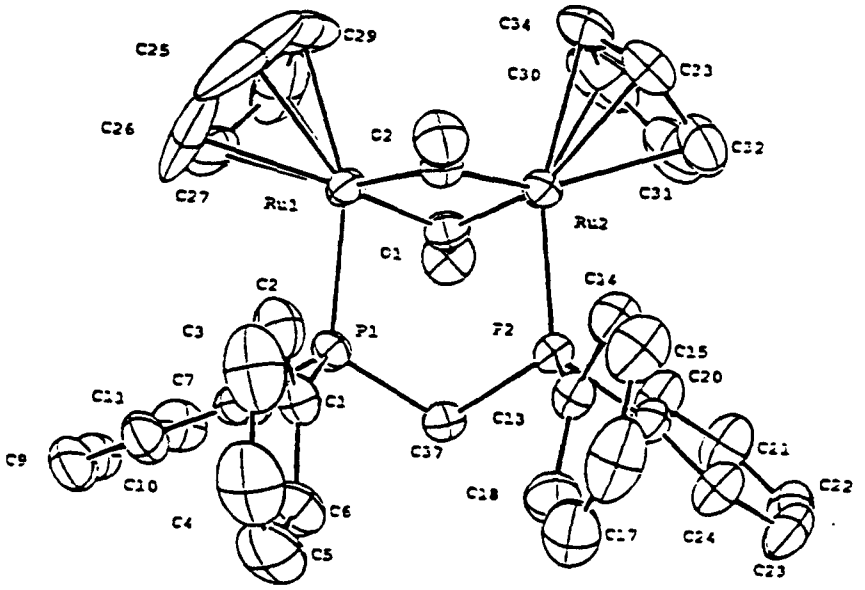


Figure 16: ORTEP of Compound VII

The major product in the phosphine dimer synthesis is a brick red compound which is believed to be a ruthenium hydride monomer. The reason for this belief is two-fold. First, the red compound remains on the alumina column during elution which indicates that it is very reactive towards the chromatographic material. Second, in the presence of chlorinated solvents ($CHCl_3$ or CH_2Cl_2) the red compound reacted to yield a dark orange compound (**IX**) which could be purified and characterized. Attempts to isolate the brick red compound initially obtained have been unsuccessful to date. Compound **IX**, $(\eta^5\text{-}C_5H_5)Ru(Cl)DPPM$, has been fully characterized through ^1H, ^{13}C and ^{31}P NMR. In addition, the structure of this monomer was confirmed by X-ray crystallography (Figure 17)[29]. A sample of compound **IX** was independently prepared through the reaction of $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ with DPPM in refluxing benzene and the proton NMR of the two samples are consistent.[30] Scheme 5 shows a possible reaction pathway for the synthesis of **IX** as a byproduct in the ruthenium phosphine dimer preparation.

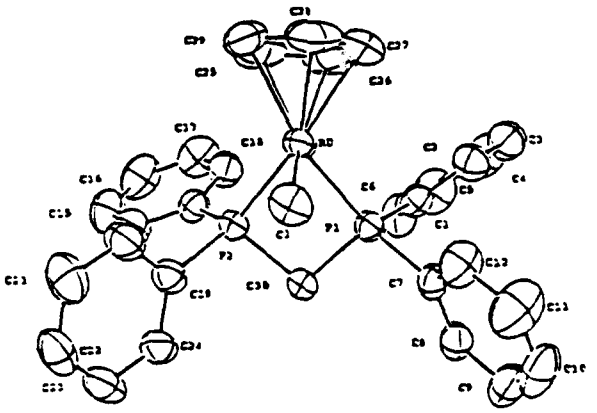
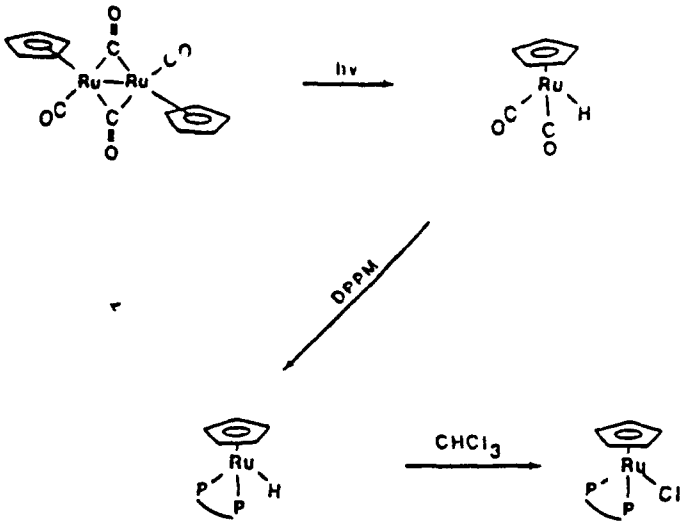


Figure 17: ORTEP of Compound **IX**



Scheme 5: Possible Synthetic Route for Compound IX

Attempts to synthesize the $(n^5\text{-}C_5H_5)_2Ru_2(u\text{-}CO)_2(u\text{-}DPPE)$ starting phosphine bridged dimer were also undertaken. To do this, an analogous photolysis reaction for synthesizing the RuDPPM dimer was used. Again the deisred product was recovered in minimal yield while the primary product, after using a chlorinated solvent in purification, was a chlorinated monomer, Compound **X**, $(n^5\text{-}C_5H_5)Ru(Cl)DPPE$. **X** has been fully chracterized by NMR analysis and its structure confirmed by X-ray crystallography (Figure 18)[29].

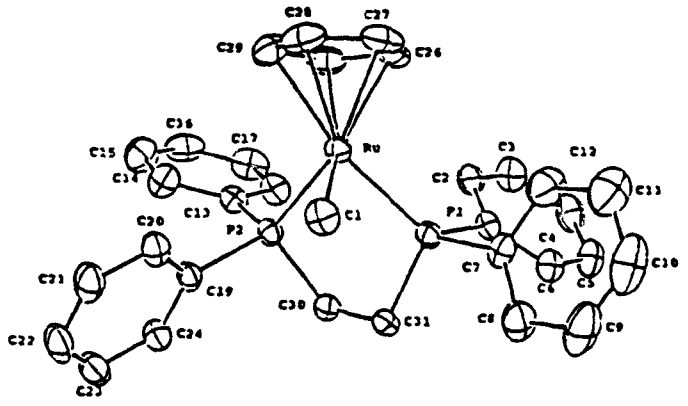


Figure 18: ORTEP of Compound **X**

After a successful synthesis of $(n^5\text{-}C_5H_5)_2Ru_2(u\text{-}CO)_2$-(u-DPPM) (VII) was developed, 0.25 g of the material was photolyzed in $CHCl_3$ under the same conditions as its iron analog. The reaction mixture changed from yellow to red-orange and the resulting oil was purified by chromatography on Grade III alumina. Trace amounts of an initial yellow band were eluted with petroleum ether/chloroform. The major product of the reaction is a red compound which required a more polar solvent mixture (chloroform/methanol) to elute the band off the column. ^1H and ^{13}C NMR spectra of the yellow band indicate the presence of a formyl group on one of the cyclopentadienyl rings in the dimer. Further structural characterization has not been accomplished due to the extremely low yield in this reaction, but the initial results indicate that the product is $(n^5\text{-}C_5H_5)(n^5\text{-}C_5H_4CHO)Ru_2(CO)_2$-(u-DPPM), Compound VIII. Additional synthesis and isolation of the yellow product is in progress.

Initial spectral results on the red compound using ^1H and ^{13}C NMR have shown that it does not contain a formyl group. These spectra indicate the presence of one type of cyclopentadienyl ring, a methylene group and phenyl groups. The IR spectrum indicates the presence of bridging carbonyls and the absence of a formyl group. Further studies are necessary to determine the composition of this compound.

Conclusion

The photolyses of the related phosphine bridged compounds $[(n^5\text{-}C_5H_5)Fe(CO)]_2$-u-DPPX, where DPPX = DPPM, DPPE and DPPP and therefore are $(Ph_2P)_2CH_2$, $(Ph_2P)_2C_2H_4$ and $(Ph_2P)_2C_3H_6$ respectively, were accomplished. In contrast to the prediction that the metal-metal bond would undergo homolysis, the photolysis DPPM and DPPE dimers in $CHCl_3$ yielded a phosphine bridged dimer containing a formyl substituted cyclopentadienyl ring. This did not occur in the photolysis of the DPPP compound and is attributed to the strain of the seven-membered ring of the molecule. Similar results were observed for the analogous ruthenium DPPM dimer. Additional experimental work is underway on the ruthenium DPPE system to synthesize the phosphine bridged dimer and ultimately the photolyzed formyl substituted product.

In the successful synthesis of ruthenium DPPM and the attempted synthesis of ruthenium DPPE, an unexpected monomeric product, $(n^5\text{-}C_5H_5)Ru(Cl)$DPPX was obtained in each reaction. These compounds were fully characterized and a possible reaction pathway has been proposed to explain their occurrence.

Subsequent work is necessary to establish whether the photochemical charge transfer reactions for the phosphine bridged dimers compete with the more familiar radical formation processes and contribute to the photochemistry of these bimetallic complexes.

Experimental

Compounds I, II, III and $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ were prepared by literature procedures.[19,26] ^1H and ^{13}C NMR spectra were recorded at ambient temperatures using a GE-QE300 Nuclear Magnetic spectrometer and referenced to solvent resonances. ^{31}P NMR spectra were recorded at ambient temperatures on the same spectrometer and referenced to 85% H_3PO_4 in a coaxial tube. IR spectra were recorded on a Perkin-Elmer 1750 Fourier Transform Infrared spectrometer. X-ray crystallographic data were collected on an Enraf Nonius FR590 diffractometer with a graphite-monochromated Mo K-alpha radiation at room temperature. Mass spectra of IV was recorded by Dr. Mark Ross of the Naval Research Laboratory and elemental analyses were performed by Desert Analytics, Inc., Tucson, AZ. Selected X-ray crystallographic data for compounds I, II, IV, V, VII, IX and X are included in Appendix A. A table of IR data (Table B-1) in the C=O and C O stretching regions for the reaction products is included in Appendix B. ^1H and ^{13}C NMR spectra for most of the compounds synthesized are included as Figures in Appendix C and ^{31}P NMR chemical shifts are listed in Appendix D (Table D-1).

Synthesis of $(n^5\text{-}C_5H_5)_2Fe_2(CO)_2(u\text{-}DPPM)$ (I)[19]

2.0 g (5.7 mMol) of $[(n^5\text{-}C_5H_5)Fe(CO)_2]_2$ was refluxed in benzene with 3.4 g (8.8 mMol) of DPPM for thirty-six hours. The solution turned green over time and the solvent was removed under vaccuum. The resultant oil was chromatographed on Grade III alumina with 1:1 petroleum ether/chloroform as the eluant to collect the green band. After removal of the solvent and crystalization from chlorofrom/pentane the product, I, was a green solid. IR:($CHCl_3$): 1670 (m). ^1H NMR: ($CDCl_3$) 7.38 - 7.18 (m, 20H, Ph), 4.05 (s, 5H, C_5H_5), 1.76 (s, 2H, CH_2), ^{13}C NMR: ($CDCl_3$) 140.53 (s, ipso Ph), 132.64 (s, ortho Ph), 129.67 (s, para Ph), 128.25 (s, meta Ph), 89.36 (s, C_5H_5), 23.40 (t, $J_{P\text{-}C}$ = 20.6 Hz, P-CH_2-P). ^{31}P NMR: ($CDCl_3$) 86.63 (s, 2P).

Synthesis of $(n^5\text{-}C_5H_5)_2Fe_2(CO)_2(u\text{-}DPPE)$ (II)[19]

2.0 g (5.7 mMol) of $[(n^5\text{-}C_5H_5)Fe(CO)_2]_2$ was refluxed in benzene with 3.4 g (8.5 mMol) of DPPE as above. After purification and crystallization from chloroform/pentane a green solid, II, resulted. IR:($CHCl_3$): 1671 (m). ^1H NMR: ($CDCl_3$) 7.70 - 7.34 (m, 20H, Ph), 4.17 (s, 5H, Cp), 1.34 (d, 4H, $J_{P\text{-}H}$ = 13.0 Hz, P-C_2H_4-P). ^{13}C NMR: ($CDCl_3$) 137.26 (s, ipso Ph), 132.95 (s, ortho Ph), 129.69 (s, para Ph), 128.22 (s, meta Ph), 86.70 (br, Cp), 22.48 (t, $J_{P\text{-}C}$ = 13.8 Hz, P-C_2H_4-P). ^{31}P NMR: ($CDCl_3$) 69.76 (s, 2P).

Synthesis of $(n^5\text{-}C_5H_5)_2Fe_2(CO)_2(u\text{-}DPPP)$ (III)[19]

2.0 g (5.7 mMol) of $[(n^5\text{-}C_5H_5)Fe(CO)_2]_2$ was refluxed in benzene with 3.4 g (8.2 mMol) of DPPP as above. After purification a green solid, III, resulted which decomposes readily in solution. Because of this decomposition, unambiguous ^{13}C NMR data could not be obtained. IR:($CHCl_3$): 1666 (m). ^1H NMR: ($CDCl_3$) 7.42 - 7.32 (m, 20H, Ph), 4.12 (s, 5H, C_5H_5), 1.73 - 0.67 (m, 6H, P-C_3H_6-P). ^{31}P NMR: ($CDCl_3$) 59.16 (s, 2P).

Synthesis of $(n^5\text{-}C_5H_5)(n^5\text{-}C_5H_4CHO)Fe_2(CO)_2(u\text{-}DPPM)$ (IV)

I, 0.50 g (0.73 mMol), was dissolved in 125 mL $CHCl_3$ in a Pyrex water-jacketed reaction vessel. The solution was then photolyzed for four hours using a 250 W General Electric sun lamp. During this time the olive green solution changed to brown. The solvent was then removed under reduced pressure and the oily product chromatographed on Grade III alumina using 6:1 petroleum ether:$CHCl_3$ as the eluant. Initially a green band of I was removed and then a golden band was subsequently removed. Solvent removal from the golden band and recrystallization from dichloromethane/pentane yielded 0.19 g of IV as a brown solid, mp: 224 - 225 °C. Yield: 37%. IR:($CHCl_3$): 1690 (m), 1682 (sh), 1658 (sh). ^1H NMR: ($CDCl_3$) 9.15 (s, 1H, CHO), 7.44 - 7.22 (m, 20H, Ph), 4.70 and 4.66 (AA'BB', 4H, C_5H_4CHO), 4.37 (s, 5H, C_5H_5), 1.89 (t, 2H, $^2J_{P\text{-}H}$ = 10.06 Hz, P-CH_2-P). ^{13}C NMR: ($CDCl_3$) 191.24 (CHO), 136.28 (dd,

ipso Ph, $^1J_{P-C}$ = 32.6 Hz, $^3J_{P-C}$ = 4.8 Hz), 135.75 (dd, ipso Ph', $^1J_{P-C}$ = 33.6 Hz, $^3J_{P-C}$ = 6.3 Hz), 132.35 (d, ortho Ph, $^2J_{P-C}$ = 9.6 Hz), 132.22 (d, ortho Ph', $^2J_{P-C}$ = 9.1 Hz), 129.96 (d, para Ph and Ph', $^4J_{P-C}$ = 8.0 Hz), 128.26 (d, meta Ph, $^3J_{P-C}$ = 9.4 Hz), 128.22 (d, meta Ph', $^3J_{P-C}$ = 9.0 Hz), 94.28 (ipso Cp), 90.37 (CHOCp), 86.91 (Cp), 85.31 (CHOCp), 28.29 (t, $^1J_{P-C}$ = 22.8 Hz). ^{31}P NMR: ($CDCl_3$) 84.48 and 81.47 (AB, $^2J_{P-P}$ = 92.38 Hz). Mass Spec: 710 (M^+), 682 (M^+ - CO), 658 (M^+ - 2CO), 589 ($CHOC_5H_4Fe_2DPPM$), 561 ($C_5H_5Fe_2DPPM$), 533 ($CHOC_5H_4FeDPPM$), 505 ($C_5H_5FeDPPM$) 440, (FeDPPM). Calcd for $C_{38}H_{32}Fe_2O_3P_2$: C, 64.25; H, 4.55; P, 8.72. Found: C, 64.36; H, 4.55; P, 8.63.

Synthesis of (η^5-C_5H_5)(η^5-C_5H_4CHO)Fe_2(CO)$_2$(u-DPPE) (V)

II, 0.50 g (0.72 mMol), was photolyzed and purified as above. V was recovered as a brown solid, mp: 243 - 244 °C decomp. Yield: 40%. IR:($CHCl_3$): 1687 (m), 1655 (sh). ^{1}H NMR: ($CDCl_3$) 8.90 (s, 1H, CHO), 7.89 (m, 8H, Ph), 7.45 (m, 12H, Ph), 4.57 and 4.53 (AA'BB', 4H, $CHOC_5H_4$), 4.72 (s, 5H, C_5H_5), 1.35 (m, 4 H, P-C_2H_4-P). ^{13}C NMR: ($CDCl_3$) 191.23 (CHO), 136.67 (broad, ipso Ph), 132.87 (broad s, ortho Ph), 130.04 (d, $^4J_{P-C}$ = 12.8 Hz, para Ph), 128.37 (pseudo t, $^3J_{P-C}$ = 8.3 Hz, meta Ph), 95.26 (ipso CHOCp), 90.37 (CHOCp), 86.88 (Cp), 84.55 (CHOCp), 22.54 (d, $^1J_{P-C}$ = 25.23 Hz, P-C_2H_4-P), 22.30 (d, $^1J_{P-C}$ = 25.72 Hz, P-C_2H_4-P). ^{31}P NMR: ($CDCl_3$) 68.52 and 64.11.

Possible synthesis of $[(\eta^5\text{-}C_5H_5)FeCl(CO)]_2(u\text{-}DPPP)$ (VI)

III, 0.50 g (0.71 mMol) was photolyzed and purified as above. VI(?) was recovered as a brown solid which decomposed in solution and also on storage. Due to the extensive decomposition, complete characterization of this compound was not accomplished. IR:($CHCl_3$) 1967 (s). ^1H NMR: ($CDCl_3$) 7.67 - 7.27 (m, 20H, Ph), 4.74 (s, 5H, C_5H_5), 3.43 - 1.99 (m, 6H, P-C_3H_6-P). ^{31}P NMR: ($CDCl_3$) 33.32 (s, 2P).

Synthesis of $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_2(u\text{-}DPPM)$ (VII)

0.50 g (0.22 mMol) of $(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_4$ and 0.60 g (0.23 mMol) of DPPM were dissolved in 125 mL benzene and then photolyzed for approximately eight to ten hours. The solvent was removed and the red product columned on Grade III alumina. Initially a 10:1 petroleum ether:benzene mixture was used to remove a small yellow band of the starting material. A petroleum ether:benzene mixture (5:3) was required to elute the golden product band. The solvent was removed from this band to yield VII which was crystallized as an orange solid from $CHCl_3$/pentane. If $CHCl_3$ or CH_2Cl_2 were used on the column, a dark orange solid also developed as a band on the column which was identified as IX. Yield 10%. IR:(C_6H_6): 1688 cm^{-1} (m). ^1H NMR: ($CDCl_3$) 7.45 - 7.21 (m, 20H, Ph), 4.89 (s, 5H, C_5H_5), 1.93 (t, 2H, $J_{P\text{-}H}$ = 9.83 Hz, P-CH_2-P). ^{13}C NMR: ($CDCl_3$) 137.47 (t, $J_{P\text{-}C}$ = 23.71 Hz, ipso Ph), 132.54 (t, $J_{P\text{-}C}$ = 5.57 Hz, ortho Ph), 129.60 (s, para Ph), 128.03 (t, $J_{P\text{-}C}$ = 4.74 Hz,

meta Ph), 89.02 (s, Cp), 22.29 (t, J_{P-C} = 24.81 Hz, P-CH_2-P). ^{31}P NMR: ($CDCl_3$) 64.99 (s, 2P).

Synthesis of (η^5-C_5H_5)(η^5-C_5H_4CHO)$Ru_2(CO)_2(\mu$-DPPM) (VIII)

0.25 g (0.32 mMol) of VII was dissolved in 125 mL $CHCl_3$ and photolyzed as above for four hours in a Pyrex water-jacketed reaction vessel. The solvent was removed under vacuum from the resultant red solution to yield a red oil which was then chromatographed on Grade III alumina using 5:1 petroleum ether:$CHCl_3$ as the eluant. The initial yellow band removed is VIII which crystallizes as a dark orange solid from $CHCl_3$/pentane. Yield 3%. IR:($CHCl_3$) 1681 (m), 1652 (sh). ^1H NMR: ($CDCl_3$) 9.108 (s, 1H, CHO), 7.46 - 7.22 (m, 20H, Ph), 5.07 and 5.01 (AA'BB', 4H, C_5H_4CHO), 4.93 (s, 5H, C_5H_5), 1.99 (t, 2H, J_{H-P} = 9.9 Hz, P-CH_2-P).

Independent Synthesis of (η^5-C_5H_5)Ru(Cl)DPPM (IX)[18]

0.37 g (0.51 mMol) of (η^5-C_5H_5)$RuCl(PPh_3)_2$ and 0.20 g (0.52 mMol) of DPPM were refluxed in 100 mL benzene for eight hours. The solvent was then removed under vacuum and the resultant oil dissolved in benzene. Hexane was added and an orange precipitate, IX, formed which was collected by filtration. Yield 76%. ^1H NMR: ($CDCl_3$) 7.75 - 7.22 (m, 20H, Ph), 5.08 (m, 1H, J_{Ha-Hb} = 14.48 Hz, J_{Ha-P} = 10.09 Hz, P-CH_2-P), 4.70 (s, 5H, C_5H_5), 4.36 (m, 1H, J_{Hb-Ha} = 14.48 Hz, J_{Hb-P} = 11.21 Hz P-CH_2-P). ^{13}C NMR: ($CDCl_3$) 138.22 (t, J_{P-C} = 20.54 Hz, ispo Ph_a), 133.75

(t, J_{P-C} = 21.97 Hz, ipso Ph_b), 132.91 (t, J_{P-C} = 5.39 Hz, ortho Ph_a), 131.76 (t, J_{P-C} = 5.38 Hz, ortho Ph_b), 129.95 (s, para Ph_a), 129.83 (s, para Ph_b), 128.52 (t, J_{P-C} = 4.86 Hz, meta Ph_a), 128.43 (t, J_{P-C} = 4.86 Hz, meta Ph_b), 78.00 (d, J_{P-C} = 2.34 Hz, Cp), 48.33 (t, J_{P-C} = 20.38 Hz, P-CH_2-P). ^{31}P NMR: ($CDCl_3$) 13.61 (s, 2P).

Independent Synthesis of (n^5-C_5H_5)Ru(Cl)DPPE (X)[18]

0.37 g (0.51 mMol) of (n^5-C_5H_5)$RuCl(PPh_3)_2$ and 0.20 g (0.51 mMol) of DPPE were refluxed and purified as above to give the desired product, X. Yield 70%. ^1H NMR: ($CDCl_3$) 7.88 - 7.15 (m, 20H, Ph), 4.54 (s, 5H, C_5H_5), 2.65 (AA'BB'XX', 2H, CH_2), 2.39 (AA'BB'XX', 2H, CH_2). ^{13}C NMR: ($CDCl_3$) 141.45 (t, J_{P-C} = 20.84 Hz, ispo Ph_a), 135.00 (t, J_{P-C} = 23.44 Hz, ipso Ph_b), 134.08 (s, ortho Ph_a), 131.69 (s, ortho Ph_b), 129.84 (s, para Ph_a), 129.27 (s, para Ph_b), 128.25 (s, meta Ph_a), 128.21 (s, meta Ph_b), 79.87 (s, Cp), 27.27 (t, J_{P-C} = 22.01 Hz, P-CH_2-P). ^{31}P NMR: ($CDCl_3$) 80.23 (s, 2P).

Method of X-ray Structure Determination

Crystal data for compounds I, II, IV, V, VII, IX and X are presented in Appendix A, Tables A-1 through A-28. Crystals of each compound were grown by evaporation of chloroform/pentane solutions. A suitable crystal was chosen for each compound and mounted in a random orientation on a glass fiber. Rotation photographs were used to locate reflections which were then indexed to obtain the unit cell for each crystal. Axial photographs confirmed axial lengths for each unit cell. Conditions of reflection were examined to confirm each space group. Linear decay corrections were applied to each data set with empirical absorption corrections based on psi scans of three reflections at 10° psi intervals.

Structures were solved using either Direct Methods or Patterson Fourier Synthesis and completed with difference Fourier synthesis. Structures were refined using full-matrix least squares modeling with anisotropic temperature factors on non-hydrogen atoms. Convergence with a shift-to-error ratio less than one percent was obtained for all structures except $(\eta^5\text{-}C_5H_5)Ru(Cl)DPPM$, which contains a disordered $CHCl_3$ solvent molecule, and $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CHO)Fe_2(CO)_2(u\text{-}DPPM)$, which contains a disordered formyl group. Further split-atom modeling is necessary for these two structures and is not complete as of this writing. Hydrogen atoms were located in the difference Fourier maps but were calculated at idealized positions and assigned a temperature factor 30% larger than

the corresponding carbon isotropic temperature factor. Hydrogen positions were updated throughout the final cycles of refinement. Examination of strong, low angle reflections revealed no extinction effects for any of the crystals.

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Appendix A

Selected Crystallographic Tables

for Compounds I, II, IV, V, VII, IX and X

Tables A-1 through A-4

for $[(n^5\text{-}C_5H_5)Fe(CO)]_2(u\text{-}DPPM)$, I

Table A-1: Crystal Data

formula	$C_{37}H_{32}O_2P_2Fe_2$
crystal system	monoclinic
space group	C2/c (No. 15)
a	23.246(1)
b	11.710(1)
c	24.047(1)
α	90
β	111.42(1)
γ	90
Volume Å^3	6093.4(7)
Z	8
D(calc) g/cm^3	1.435
D(obs) g/cm^3	1.489
u(Mo Kα) cm^{-1}	10.85
temp K	296
crystal size,mm	0.25 x 0.35 x 0.50
crystal color	dk. green
	(ii) Data Collection
diffractometer	Enraf-Nonius CAD4
monochromator	oriented graphite
radiation	Mo Kα
wavelength	0.71073
2Θ limits, deg	2-50
scan technique	Θ-2Θ
standards	3 std/100 refls
decay (max)	0.67 %
octants collcd	±h, ±k, ±l (1-20° 2Θ) h, ±k,±l (20-30° 2Θ) h, k, ±l (30-50° 2Θ)
no.of rflns collcd	7470
no of independt rflns	5457
no of independt rflns Fo ≥ 3σ (Fo)	4222
R(I) on averaging	1.0 %
T(max)/T(min)	1.04
	(iii) Refinement
R(F), %	3.0
$R_w(F)$, %	3.6
GOF	1.902
Δ/σ	0.01
Δ(ρ), e Å^{-3}	0.262
N_o/N_v	11/1

Table A-2: Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe1	Fe2	2.5188(6)	P2	C19	1.844(2)
Fe1	P1	2.1763(6)	O1	C35	1.194(3)
Fe1	C35	1.903(2)	O2	C36	1.187(2)
Fe1	C36	1.909(2)	C27	C26	1.317(4)
Fe1	C27	2.096(4)	C27	C28	1.432(6)
Fe1	C26	2.106(4)	C26	C25	1.296(5)
Fe1	C25	2.120(3)	C25	C29	1.333(5)
Fe1	C29	2.092(3)	C29	C28	1.425(5)
Fe1	C28	2.081(4)	C33	C34	1.388(5)
Fe2	P2	2.1914(6)	C33	C32	1.365(4)
Fe2	C35	1.900(3)	C34	C30	1.402(4)
Fe2	C36	1.906(2)	C30	C31	1.398(6)
Fe2	C33	2.125(3)	C31	C32	1.387(5)
Fe2	C34	2.109(3)	C7	C8	1.384(4)
Fe2	C30	2.094(3)	C7	C12	1.388(3)
Fe2	C31	2.106(4)	C8	C9	1.384(4)
Fe2	C32	2.110(4)	C9	C10	1.365(4)
P1	C37	1.835(2)	C10	C11	1.368(5)
P1	C7	1.839(3)	C11	C12	1.379(4)
P1	C1	1.836(2)	C1	C6	1.394(3)
P2	C37	1.844(3)	C1	C2	1.383(3)
P2	C13	1.837(2)	C6	C5	1.372(4)
C5	C4	1.371(4)	C17	C18	1.379(4)
C4	C3	1.365(4)	C19	C24	1.384(4)
C3	C2	1.389(4)	C19	C20	1.377(3)
C13	C14	1.380(3)	C24	C23	1.381(4)
C13	C18	1.381(3)	C23	C22	1.360(4)
C14	C15	1.382(4)	C22	C21	1.362(5)
C15	C16	1.363(4)	C21	C20	1.389(4)
C16	C17	1.365(4)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-3: Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Fe2	Fe1	P1	96.51(2)	C36	Fe1	C26	124.1(1)
Fe2	Fe1	C35	48.48(8)	C36	Fe1	C25	93.9(1)
Fe2	Fe1	C36	48.64(7)	C36	Fe1	C29	92.6(1)
Fe2	Fe1	C27	145.6(1)	C36	Fe1	C28	126.0(2)
Fe2	Fe1	C26	168.52(9)	C27	Fe1	C26	36.5(1)
Fe2	Fe1	C25	133.0(1)	C27	Fe1	C25	61.4(1)
Fe2	Fe1	C29	107.7(1)	C27	Fe1	C29	64.3(1)
Fe2	Fe1	C28	111.3(1)	C27	Fe1	C28	40.1(2)
P1	Fe1	C35	87.66(7)	C26	Fe1	C25	35.7(1)
P1	Fe1	C36	92.43(7)	C26	Fe1	C29	61.8(1)
P1	Fe1	C27	103.1(1)	C26	Fe1	C28	64.3(2)
P1	Fe1	C26	92.6(1)	C25	Fe1	C29	36.9(1)
P1	Fe1	C25	114.9(1)	C25	Fe1	C28	64.2(1)
P1	Fe1	C29	151.6(1)	C29	Fe1	C28	39.9(1)
P1	Fe1	C28	141.4(1)	Fe1	Fe2	P2	95.82(2)
C35	Fe1	C36	96.5(1)	Fe1	Fe2	C35	48.59(7)
C35	Fe1	C27	104.0(1)	Fe1	Fe2	C36	48.72(8)
C35	Fe1	C26	139.3(1)	Fe1	Fe2	C33	128.95(9)
C35	Fe1	C25	154.8(1)	Fe1	Fe2	C34	103.9(1)
C35	Fe1	C29	119.4(1)	Fe1	Fe2	C30	111.2(1)
C35	Fe1	C28	91.2(1)	Fe1	Fe2	C31	144.8(1)
C36	Fe1	C27	154.6(1)	Fe1	Fe2	C32	166.49(7)
P2	Fe2	C35	88.44(7)	C34	Fe2	C30	39.0(1)
P2	Fe2	C36	90.69(7)	C34	Fe2	C31	65.1(1)
P2	Fe2	C33	118.20(9)	C34	Fe2	C32	64.3(1)
P2	Fe2	C34	156.3(1)	C30	Fe2	C31	38.9(2)
P2	Fe2	C30	142.1(1)	C30	Fe2	C32	64.5(2)
P2	Fe2	C31	105.13(9)	C31	Fe2	C32	38.4(1)
P2	Fe2	C32	94.29(9)	Fe1	P1	C37	111.32(8)
C35	Fe2	C36	96.7(1)	Fe1	P1	C7	113.79(8)
C35	Fe2	C33	152.1(1)	Fe1	P1	C1	121.58(7)
C35	Fe2	C34	114.5(1)	C37	P1	C7	104.4(1)
C35	Fe2	C30	90.2(1)	C37	P1	C1	101.2(1)
C35	Fe2	C31	103.3(1)	C7	P1	C1	102.5(1)
C35	Fe2	C32	140.8(1)	Fe2	P2	C37	110.60(8)
C36	Fe2	C33	91.4(1)	Fe2	P2	C13	118.85(7)
C36	Fe2	C34	92.5(1)	Fe2	P2	C19	118.22(8)
C36	Fe2	C30	127.0(1)	C37	P2	C13	103.7(1)
C36	Fe2	C31	154.7(1)	C37	P2	C19	101.5(1)
C36	Fe2	C32	122.3(1)	C13	P2	C19	101.7(1)
C33	Fe2	C34	38.3(1)	P1	C37	P2	108.7(1)
C33	Fe2	C30	64.0(1)	Fe1	C35	Fe2	82.94(8)
C33	Fe2	C31	63.8(1)	Fe1	C35	O1	138.8(2)
C33	Fe2	C32	37.6(1)	Fe2	C35	O1	138.1(2)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Fe1	C36	Fe2	82.64(8)	Fe2	C34	C30	69.9(2)
Fe1	C36	O2	138.6(2)	C33	C34	C30	106.6(3)
Fe2	C36	O2	137.7(2)	Fe2	C30	C34	71.1(2)
Fe1	C27	C26	72.1(2)	Fe2	C30	C31	71.0(2)
Fe1	C27	C28	69.4(2)	C34	C30	C31	108.2(3)
C26	C27	C28	108.1(3)	Fe2	C31	C30	70.1(2)
Fe1	C26	C27	71.3(2)	Fe2	C31	C32	70.9(2)
Fe1	C26	C25	72.7(2)	C30	C31	C32	107.2(3)
C27	C26	C25	111.0(3)	Fe2	C32	C33	71.8(2)
Fe1	C25	C26	71.5(2)	Fe2	C32	C31	70.6(2)
Fe1	C25	C29	70.4(2)	C33	C32	C31	108.6(3)
C26	C25	C29	110.2(3)	P1	C7	C8	122.1(2)
Fe1	C29	C25	72.7(2)	P1	C7	C12	119.2(2)
Fe1	C29	C28	69.6(2)	C8	C7	C12	118.2(2)
C25	C29	C28	108.1(3)	C7	C8	C9	120.4(2)
Fe1	C28	C27	70.5(2)	C8	C9	C10	120.5(3)
Fe1	C28	C29	70.5(2)	C9	C10	C11	119.8(3)
C27	C28	C29	102.5(3)	C10	C11	C12	120.3(2)
Fe2	C33	C34	70.3(2)	C7	C12	C11	120.7(3)
Fe2	C33	C32	70.6(2)	P1	C1	C6	120.5(2)
C34	C33	C32	109.4(2)	P1	C1	C2	120.6(2)
Fe2	C34	C33	71.5(2)	C6	C1	C2	118.8(2)
C1	C6	C5	120.4(2)	C16	C17	C18	119.8(3)
C6	C5	C4	120.3(3)	C13	C18	C17	120.9(2)
C5	C4	C3	120.1(3)	P2	C19	C24	123.5(2)
C4	C3	C2	120.4(2)	P2	C19	C20	118.5(2)
C1	C2	C3	119.9(2)	C24	C19	C20	117.9(2)
P2	C13	C14	119.2(2)	C19	C24	C23	120.6(2)
P2	C13	C18	122.5(2)	C24	C23	C22	120.8(3)
C14	C13	C18	118.3(2)	C23	C22	C21	119.6(2)
C13	C14	C15	120.6(2)	C22	C21	C20	120.2(3)
C14	C15	C16	120.0(2)	C19	C20	C21	120.9(3)
C15	C16	C17	120.3(3)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-4: Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Fe1	0.59805(1)	0.05814(3)	0.65000(1)	2.505(7)
Fe2	0.67344(1)	0.04177(3)	0.59722(1)	2.576(7)
P1	0.62965(2)	0.22362(5)	0.69091(2)	2.24(1)
P2	0.71741(2)	0.20800(5)	0.62626(3)	2.22(1)
O1	0.72087(8)	-0.0243(2)	0.72218(8)	4.16(5)
O2	0.55639(7)	0.1485(2)	0.52906(7)	3.58(4)
C37	0.7091(1)	0.2529(2)	0.6965(1)	2.50(5)
C35	0.6824(1)	0.0123(2)	0.6777(1)	2.92(5)
C36	0.5936(1)	0.1101(2)	0.5733(1)	2.62(5)
C27	0.5634(2)	-0.0195(3)	0.7098(1)	6.11(8)
C26	0.5226(1)	0.0564(3)	0.6786(2)	6.16(8)
C25	0.5015(1)	0.0308(3)	0.6222(2)	6.18(9)
C29	0.5287(1)	-0.0636(3)	0.6130(1)	7.38(8)
C28	0.5712(2)	-0.1020(3)	0.6692(2)	9.1(1)
C33	0.6572(1)	-0.0116(3)	0.5083(1)	4.49(7)
C34	0.6401(2)	-0.0977(3)	0.5388(1)	5.25(7)
C30	0.6937(2)	-0.1292(3)	0.5867(2)	6.9(1)
C31	0.7424(1)	-0.0608(3)	0.5852(2)	6.57(9)
C32	0.7185(1)	0.0121(3)	0.5366(1)	5.14(7)
C7	0.6325(1)	0.2352(2)	0.7682(1)	2.72(5)
C8	0.5927(1)	0.3053(2)	0.7835(1)	3.63(6)
C9	0.5920(1)	0.3032(3)	0.8408(1)	4.31(6)
C10	0.6297(1)	0.2304(3)	0.8827(1)	4.28(6)
C11	0.6689(1)	0.1598(3)	0.8681(1)	4.32(7)
C12	0.6705(1)	0.1619(2)	0.8113(1)	3.78(6)
C1	0.5906(1)	0.3565(2)	0.6569(1)	2.81(5)
C6	0.6146(1)	0.4620(2)	0.6813(1)	4.04(6)
C5	0.5869(2)	0.5613(3)	0.6543(2)	5.36(8)
C4	0.5355(2)	0.5578(3)	0.6028(2)	5.64(8)
C3	0.5117(1)	0.4554(3)	0.5779(1)	4.92(7)
C2	0.5385(1)	0.3539(2)	0.6051(1)	3.47(6)
C13	0.68950(9)	0.3318(2)	0.5768(1)	2.61(5)
C14	0.6593(1)	0.3144(2)	0.5163(1)	3.18(5)
C15	0.6397(1)	0.4059(3)	0.4776(1)	4.18(6)
C16	0.6494(1)	0.5147(3)	0.4992(1)	4.52(7)
C17	0.6788(1)	0.5338(2)	0.5590(1)	4.39(7)
C18	0.6988(1)	0.4427(2)	0.5977(1)	3.56(6)
C19	0.8017(1)	0.2191(2)	0.6461(1)	2.64(5)
C24	0.8297(1)	0.3054(2)	0.6259(1)	3.46(6)
C23	0.8933(1)	0.3094(3)	0.6430(1)	4.33(6)
C22	0.9295(1)	0.2275(3)	0.6792(1)	4.18(7)
C21	0.9028(1)	0.1414(3)	0.6993(1)	4.61(7)
C20	0.8390(1)	0.1368(3)	0.6827(1)	3.99(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Tables A-5 through A-8

for $[(n^5\text{-}C_5H_5)Fe(CO)]_2(u\text{-}DPPE)$, II

Table A-5: Crystal Data

formula	$C_{38}H_{36}O_2P_2Fe_2$
crystal system	rhombohedral
space group	$R\bar{3}$ (No. 148)
a	27.749(2)
b	27.749(2)
c	27.749(2)
α	116.52(9)
β	116.52(9)
γ	116.52(9)
Volume Å^3	10104(15)
Z	12[a]
D(calc) g/cm^3	1.373
D(obs) g/cm^3	1.410
u(Mo Kα) cm^{-1}	10.5
temp K	296
crystal size,mm	0.30 x 0.20 x 0.25
crystal color	dark green
	(ii) Data Collection
diffractometer	Enraf-Nonius CAD4
monochromator	oriented graphite
radiation	Mo Kα
wavelength	0.71073
2Θ limits, deg	2-50
scan technique	ω
standards	3 std/100 refls
decay (max)	4.2 %
octants collcd	± h,k,±l (1-30° 2Θ) h,k,±l (30-50° 2Θ)
no.of rflns collcd	17970
no of independt rflns	13477
no of independt rflns Fo ≥ 3σ (Fo)	5419
R(I) on averaging	3.8 %
T(max)/T(min)	1.02
	(iii) Refinement
R(F), %	4.1
R_w(F), %	5.9
GOF	1.937
Δ/σ	0.01
Δ(ρ), e Å^{-3}	2.52 near Fe 0.87 near light atoms
N_o/N_v	6.83

a This is the number of molecules in the unit cell. The number of asymmetric units per unit cell is 6, with 2 molecules per asymmetric unit.

Table A-6: Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe1	Fe2	2.516(1)	P2	C38	1.838(8)
Fe1	P1	2.172(2)	O1	C35	1.181(8)
Fe1	C25	2.126(3)	O2	C36	1.202(8)
Fe1	C26	2.095(7)	C1	C2	1.368(5)
Fe1	C27	2.101(8)	C1	C6	1.39(1)
Fe1	C28	2.118(8)	C2	C3	1.38(1)
Fe1	C29	2.136(6)	C3	C4	1.38(1)
Fe1	C35	1.922(4)	C4	C5	1.359(7)
Fe1	C36	1.884(8)	C5	C6	1.39(1)
Fe2	P2	2.180(2)	C7	C8	1.39(1)
Fe2	C30	2.133(8)	C7	C12	1.37(1)
Fe2	C31	2.127(9)	C8	C9	1.40(1)
Fe2	C32	2.102(8)	C9	C10	1.36(1)
Fe2	C33	2.105(9)	C10	C11	1.35(1)
Fe2	C34	2.119(7)	C11	C12	1.38(1)
Fe2	C35	1.908(8)	C13	C14	1.38(1)
Fe2	C36	1.902(6)	C13	C18	1.400(9)
P1	C1	1.841(7)	C14	C15	1.38(1)
P1	C7	1.825(8)	C15	C16	1.37(1)
P1	C37	1.825(4)	C16	C17	1.37(1)
P2	C13	1.830(8)	C17	C18	1.37(1)
P2	C19	1.843(3)	C19	C20	1.40(1)
C19	C24	1.385(8)	Fe1'	C29'	2.119(8)
C20	C21	1.379(5)	Fe1'	C35'	1.918(8)
C21	C22	1.36(1)	Fe1'	C36'	1.906(7)
C22	C23	1.36(1)	Fe2'	P2'	2.177(2)
C23	C24	1.361(5)	Fe2'	C34'	2.124(7)
C25	C26	1.41(1)	Fe2'	C33'	2.113(5)
C25	C29	1.40(1)	Fe2'	C32'	2.089(6)
C26	C27	1.42(1)	Fe2'	C31'	2.120(8)
C27	C28	1.39(1)	Fe2'	C30'	2.141(7)
C28	C29	1.42(1)	Fe2'	C35'	1.887(6)
C30	C31	1.390(4)	Fe2'	C36'	1.913(8)
C30	C34	1.41(1)	P1'	C1'	1.842(8)
C31	C32	1.38(1)	P1'	C7'	1.829(6)
C32	C33	1.408(7)	P1'	C37'	1.816(9)
C33	C34	1.413(9)	P2'	C13'	1.832(8)
C37	C38	1.51(1)	P2'	C19'	1.832(9)
Fe1'	Fe2'	2.512(1)	P2'	C38'	1.831(5)
Fe1'	P1'	2.182(2)	O1'	C35'	1.19(1)
Fe1'	C28'	2.108(9)	O2'	C36'	1.18(1)
Fe1'	C27'	2.105(9)	C1'	C2'	1.36(1)
Fe1'	C26'	2.093(8)	C1'	C6'	1.405(8)
Fe1'	C25'	2.128(9)	C2'	C3'	1.38(1)

Bond Distances (cont.)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
C3'	C4'	1.339(9)	C19'	C24'	1.39(1)
C4'	C5'	1.38(2)	C20'	C21'	1.39(1)
C5'	C6'	1.36(1)	C21'	C22'	1.38(1)
C7'	C8'	1.376(8)	C22'	C23'	1.37(1)
C7'	C12'	1.40(1)	C23'	C24'	1.38(1)
C8'	C9'	1.38(1)	C34'	C33'	1.41(1)
C9'	C10'	1.36(1)	C34'	C30'	1.38(2)
C10'	C11'	1.37(1)	C33'	C32'	1.41(2)
C11'	C12'	1.37(1)	C32'	C31'	1.38(1)
C13'	C14'	1.40(1)	C31'	C30'	1.39(1)
C13'	C18'	1.40(1)	C28'	C27'	1.391(4)
C14'	C15'	1.37(1)	C28'	C29'	1.37(1)
C15'	C16'	1.35(2)	C27'	C26'	1.40(1)
C16'	C17'	1.38(1)	C26'	C25'	1.390(9)
C17'	C18'	1.38(1)	C25'	C29'	1.394(9)
C19'	C20'	1.37(1)	C37'	C38'	1.540(9)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-7: Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Fe2	Fe1	P1	105.64(6)	C26	Fe1	C28	65.4(3)
Fe2	Fe1	C25	127.1(3)	C26	Fe1	C29	64.8(3)
Fe2	Fe1	C26	165.2(2)	C26	Fe1	C35	139.1(3)
Fe2	Fe1	C27	139.5(2)	C26	Fe1	C36	126.0(2)
Fe2	Fe1	C28	106.2(2)	C27	Fe1	C28	38.5(3)
Fe2	Fe1	C29	100.8(2)	C27	Fe1	C29	64.7(3)
Fe2	Fe1	C35	48.7(2)	C27	Fe1	C35	101.2(3)
Fe2	Fe1	C36	48.7(2)	C27	Fe1	C36	158.7(1)
P1	Fe1	C25	114.1(3)	C28	Fe1	C29	39.0(3)
P1	Fe1	C26	87.9(2)	C28	Fe1	C35	89.6(3)
P1	Fe1	C27	100.1(2)	C28	Fe1	C36	128.9(3)
P1	Fe1	C28	137.4(3)	C29	Fe1	C35	115.4(3)
P1	Fe1	C29	151.4(2)	C29	Fe1	C36	95.8(3)
P1	Fe1	C35	90.6(2)	C35	Fe1	C36	94.9(3)
P1	Fe1	C36	93.5(2)	Fe1	Fe2	P2	105.65(7)
C25	Fe1	C26	39.0(3)	Fe1	Fe2	C30	99.6(2)
C25	Fe1	C27	65.3(3)	Fe1	Fe2	C31	125.7(2)
C25	Fe1	C28	65.1(3)	Fe1	Fe2	C32	163.3(3)
C25	Fe1	C29	38.3(3)	Fe1	Fe2	C33	140.55(8)
C25	Fe1	C35	153.0(3)	Fe1	Fe2	C34	106.1(2)
C25	Fe1	C36	94.3(3)	Fe1	Fe2	C35	49.2(1)
C26	Fe1	C27	39.4(3)	Fe1	Fe2	C36	48.1(2)
P2	Fe2	C30	153.1(2)	C33	Fe2	C34	39.1(3)
P2	Fe2	C31	116.2(1)	C33	Fe2	C35	158.0(3)
P2	Fe2	C32	89.5(2)	C33	Fe2	C36	102.7(3)
P2	Fe2	C33	99.4(2)	C34	Fe2	C35	129.4(3)
P2	Fe2	C34	136.8(3)	C34	Fe2	C36	89.4(3)
P2	Fe2	C35	93.7(2)	C35	Fe2	C36	94.7(3)
P2	Fe2	C36	90.6(2)	Fe1	P1	C1	117.1(2)
C30	Fe2	C31	38.1(2)	Fe1	P1	C7	112.7(3)
C30	Fe2	C32	64.4(3)	Fe1	P1	C37	117.6(3)
C30	Fe2	C33	65.0(3)	C1	P1	C7	103.8(4)
C30	Fe2	C34	38.6(3)	C1	P1	C37	102.2(3)
C30	Fe2	C35	95.9(3)	C7	P1	C37	101.3(3)
C30	Fe2	C36	113.6(2)	Fe2	P2	C13	114.1(2)
C31	Fe2	C32	38.2(4)	Fe2	P2	C19	117.6(3)
C31	Fe2	C33	64.7(3)	Fe2	P2	C38	119.5(2)
C31	Fe2	C34	64.3(2)	C13	P2	C19	102.9(3)
C31	Fe2	C35	93.7(3)	C13	P2	C38	99.5(4)
C31	Fe2	C36	151.3(2)	C19	P2	C38	100.3(3)
C32	Fe2	C33	39.1(2)	P1	C1	C2	120.1(6)
C32	Fe2	C34	65.1(2)	P1	C1	C6	121.8(5)
C32	Fe2	C35	124.2(3)	C2	C1	C6	118.1(7)
C32	Fe2	C36	141.0(3)	C1	C2	C3	121.1(7)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C3	C4	120.1(5)	C20	C19	C24	117.4(4)
C3	C4	C5	119.9(8)	C19	C20	C21	120.4(6)
C4	C5	C6	119.5(8)	C20	C21	C22	120.7(8)
C1	C6	C5	121.2(4)	C21	C22	C23	119.1(4)
P1	C7	C8	122.8(5)	C22	C23	C24	121.4(6)
P1	C7	C12	119.3(6)	C19	C24	C23	120.9(8)
C8	C7	C12	117.6(8)	Fe1	C25	C26	69.3(2)
C7	C8	C9	120.3(8)	Fe1	C25	C29	71.2(2)
C8	C9	C10	120.0(9)	C26	C25	C29	107.9(7)
C9	C10	C11	120(1)	Fe1	C26	C25	71.7(4)
C10	C11	C12	120.1(9)	Fe1	C26	C27	70.5(4)
C7	C12	C11	121.7(8)	C25	C26	C27	107.7(8)
P2	C13	C14	123.3(5)	Fe1	C27	C26	70.1(5)
P2	C13	C18	119.4(5)	Fe1	C27	C28	71.4(5)
C14	C13	C18	117.2(7)	C26	C27	C28	108.5(7)
C13	C14	C15	120.9(6)	Fe1	C28	C27	70.1(5)
C14	C15	C16	119.9(8)	Fe1	C28	C29	71.2(5)
C15	C16	C17	120.8(9)	C27	C28	C29	107.6(7)
C16	C17	C18	118.9(7)	Fe1	C29	C25	70.5(4)
C13	C18	C17	122.0(6)	Fe1	C29	C28	69.8(3)
P2	C19	C20	120.0(4)	C25	C29	C28	108.3(8)
P2	C19	C24	122.5(6)	Fe2	C30	C31	70.7(5)
Fe2	C30	C34	70.1(5)	Fe2'	Fe1'	P1'	106.27(7)
C31	C30	C34	107.9(7)	Fe2'	Fe1'	C28'	103.7(1)
Fe2	C31	C30	71.2(5)	Fe2'	Fe1'	C27'	136.5(2)
Fe2	C31	C32	69.9(5)	Fe2'	Fe1'	C26'	164.0(2)
C30	C31	C32	108.8(6)	Fe2'	Fe1'	C25'	127.8(1)
Fe2	C32	C31	71.9(5)	Fe2'	Fe1'	C29'	99.7(1)
Fe2	C32	C33	70.6(5)	Fe2'	Fe1'	C35'	48.1(2)
C31	C32	C33	108.3(5)	Fe2'	Fe1'	C36'	49.0(2)
Fe2	C33	C32	70.3(5)	P1'	Fe1'	C28'	139.2(1)
Fe2	C33	C34	71.0(5)	P1'	Fe1'	C27'	101.7(1)
C32	C33	C34	107.1(7)	P1'	Fe1'	C26'	89.3(2)
Fe2	C34	C30	71.3(4)	P1'	Fe1'	C25'	114.5(1)
Fe2	C34	C33	69.9(4)	P1'	Fe1'	C29'	152.0(2)
C30	C34	C33	107.8(4)	P1'	Fe1'	C35'	90.0(2)
Fe1	C35	Fe2	82.1(2)	P1'	Fe1'	C36'	94.1(2)
Fe1	C35	O1	137.2(6)	C28'	Fe1'	C27'	38.6(2)
Fe2	C35	O1	140.3(5)	C28'	Fe1'	C26'	64.5(3)
Fe1	C36	Fe2	83.3(3)	C28'	Fe1'	C25'	63.9(4)
Fe1	C36	O2	138.8(5)	C28'	Fe1'	C29'	37.8(3)
Fe2	C36	O2	137.2(6)	C28'	Fe1'	C35'	89.8(3)
P1	C37	C38	111.4(3)	C28'	Fe1'	C36'	126.5(2)
P2	C38	C37	114.0(6)	C27'	Fe1'	C26'	38.9(4)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C27'	Fe1'	C25'	64.6(4)	P2'	Fe2'	C34'	134.1(3)
C27'	Fe1'	C29'	64.2(3)	P2'	Fe2'	C33'	97.4(3)
C27'	Fe1'	C35'	100.1(4)	P2'	Fe2'	C32'	89.9(3)
C27'	Fe1'	C36'	158.5(3)	P2'	Fe2'	C31'	118.6(3)
C26'	Fe1'	C25'	38.4(3)	P2'	Fe2'	C30'	154.3(2)
C26'	Fe1'	C29'	64.3(2)	P2'	Fe2'	C35'	92.8(2)
C26'	Fe1'	C35'	137.5(4)	P2'	Fe2'	C36'	90.3(2)
C26'	Fe1'	C36'	128.1(4)	C34'	Fe2'	C33'	38.8(4)
C25'	Fe1'	C29'	38.3(3)	C34'	Fe2'	C32'	64.6(3)
C25'	Fe1'	C35'	152.7(3)	C34'	Fe2'	C31'	63.7(4)
C25'	Fe1'	C36'	95.7(3)	C34'	Fe2'	C30'	37.8(4)
C29'	Fe1'	C35'	115.4(3)	C34'	Fe2'	C35'	132.8(4)
C29'	Fe1'	C36'	95.2(3)	C34'	Fe2'	C36'	90.1(3)
C35'	Fe1'	C36'	94.3(3)	C33'	Fe2'	C32'	39.3(4)
Fe1'	Fe2'	P2'	105.73(4)	C33'	Fe2'	C31'	64.8(3)
Fe1'	Fe2'	C34'	108.6(2)	C33'	Fe2'	C30'	64.8(3)
Fe1'	Fe2'	C33'	143.8(3)	C33'	Fe2'	C35'	157.4(3)
Fe1'	Fe2'	C32'	161.2(3)	C33'	Fe2'	C36'	104.9(3)
Fe1'	Fe2'	C31'	122.9(2)	C32'	Fe2'	C31'	38.4(4)
Fe1'	Fe2'	C30'	99.1(2)	C32'	Fe2'	C30'	64.5(3)
Fe1'	Fe2'	C35'	49.2(2)	C32'	Fe2'	C35'	121.1(4)
Fe1'	Fe2'	C36'	48.7(2)	C32'	Fe2'	C36'	143.7(3)
C31'	Fe2'	C30'	38.2(4)	C2'	C3'	C4'	120.3(9)
C31'	Fe2'	C35'	92.6(3)	C3'	C4'	C5'	120.1(9)
C31'	Fe2'	C36'	149.7(3)	C4'	C5'	C6'	120.3(6)
C30'	Fe2'	C35'	98.3(3)	C1'	C6'	C5'	120.4(8)
C30'	Fe2'	C36'	111.6(4)	P1'	C7'	C8'	124.0(7)
C35'	Fe2'	C36'	95.1(3)	P1'	C7'	C12'	119.0(4)
Fe1'	P1'	C1'	118.8(2)	C8'	C7'	C12'	116.9(6)
Fe1'	P1'	C7'	112.9(2)	C7'	C8'	C9'	122.3(8)
Fe1'	P1'	C37'	118.3(1)	C8'	C9'	C10'	119.2(6)
C1'	P1'	C7'	101.6(3)	C9'	C10'	C11'	120.0(8)
C1'	P1'	C37'	101.5(4)	C10'	C11'	C12'	121(1)
C7'	P1'	C37'	101.2(3)	C7'	C12'	C11'	120.5(7)
Fe2'	P2'	C13'	114.4(2)	P2'	C13'	C14'	121.5(7)
Fe2'	P2'	C19'	119.8(3)	P2'	C13'	C18'	119.5(6)
Fe2'	P2'	C38'	116.7(3)	C14'	C13'	C18'	118.7(7)
C13'	P2'	C19'	101.3(4)	C13'	C14'	C15'	120.6(9)
C13'	P2'	C38'	102.6(3)	C14'	C15'	C16'	120.5(8)
C19'	P2'	C38'	99.3(3)	C15'	C16'	C17'	120.4(9)
P1'	C1'	C2'	121.7(4)	C16'	C17'	C18'	120.(1)
P1'	C1'	C6'	120.8(6)	C13'	C18'	C17'	119.3(8)
C2'	C1'	C6'	117.5(7)	P2'	C19'	C20'	121.7(6)
C1'	C2'	C3'	121.3(6)	P2'	C19'	C24'	120.7(7)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C20'	C19'	C24'	117.6(8)	Fe1'	C28'	C29'	71.5(5)
C19'	C20'	C21'	121.3(8)	C27'	C28'	C29'	108.9(7)
C20'	C21'	C22'	120.5(9)	Fe1'	C27'	C28'	70.8(5)
C21'	C22'	C23'	118.8(9)	Fe1'	C27'	C26'	70.0(5)
C22'	C23'	C24'	120.4(9)	C28'	C27'	C26'	106.9(7)
C19'	C24'	C23'	121.3(9)	Fe1'	C26'	C27'	71.0(5)
Fe2'	C34'	C33'	70.2(4)	Fe1'	C26'	C25'	72.2(4)
Fe2'	C34'	C30'	71.7(4)	C27'	C26'	C25'	108.4(5)
C33'	C34'	C30'	109.5(9)	Fe1'	C25'	C26'	69.4(5)
Fe2'	C33'	C34'	71.0(3)	Fe1'	C25'	C29'	70.5(5)
Fe2'	C33'	C32'	69.4(3)	C26'	C25'	C29'	107.3(8)
C34'	C33'	C32'	105.9(9)	Fe1'	C29'	C28'	70.7(5)
Fe2'	C32'	C33'	71.2(4)	Fe1'	C29'	C25'	71.2(5)
Fe2'	C32'	C31'	72.0(4)	C28'	C29'	C25'	108.5(4)
C33'	C32'	C31'	108.4(9)	Fe1'	C35'	Fe2'	82.6(3)
Fe2'	C31'	C32'	69.6(4)	Fe1'	C35'	O1'	136.2(5)
Fe2'	C31'	C30'	71.7(5)	Fe2'	C35'	O1'	140.5(5)
C32'	C31'	C30'	108.8(9)	Fe1'	C36'	Fe2'	82.3(3)
Fe2'	C30'	C34'	70.4(5)	Fe1'	C36'	O2'	138.6(5)
Fe2'	C30'	C31'	70.1(4)	Fe2'	C36'	O2'	138.8(4)
C34'	C30'	C31'	107.4(9)	P1'	C37'	C38'	112.5(5)
Fe1'	C28'	C27'	70.6(5)	P2'	C38'	C37'	111.4(5)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-8: Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Fe1	0.93969(3)	-0.22790(3)	0.33589(3)	2.45(2)
Fe2	0.82777(3)	-0.25438(4)	0.23588(4)	2.61(2)
P1	0.92236(6)	-0.31797(6)	0.25043(6)	2.43(4)
P2	0.76605(7)	-0.34871(7)	0.10685(7)	2.68(5)
O1	0.7520(2)	-0.3914(2)	0.2104(2)	3.9(1)
O2	1.0006(2)	-0.1271(2)	0.3201(2)	3.7(1)
C1	1.0098(2)	-0.2658(2)	0.2681(2)	2.6(2)
C2	1.0883(3)	-0.1729(3)	0.3412(3)	3.6(2)
C3	1.1545(3)	-0.1324(3)	0.3554(3)	4.8(3)
C4	1.1419(3)	-0.1855(3)	0.2951(3)	5.2(3)
C5	1.0636(3)	-0.2779(3)	0.2209(3)	5.0(2)
C6	0.9974(3)	-0.3182(3)	0.2072(3)	3.9(2)
C7	0.9199(3)	-0.3775(2)	0.2636(3)	2.9(2)
C8	0.9900(3)	-0.3585(3)	0.3058(3)	4.8(2)
C9	0.9885(3)	-0.4000(3)	0.3217(4)	6.6(3)
C10	0.9177(4)	-0.4603(3)	0.2947(4)	6.7(3)
C11	0.8498(4)	-0.4781(3)	0.2549(3)	6.1(3)
C12	0.8504(3)	-0.4378(3)	0.2387(3)	4.5(2)
C13	0.7764(3)	-0.3071(3)	0.0715(2)	2.9(2)
C14	0.7071(3)	-0.3334(3)	0.0080(3)	3.9(2)
C15	0.7188(3)	-0.2993(3)	-0.0157(3)	4.9(2)
C16	0.7995(3)	-0.2398(3)	0.0228(3)	5.0(2)
C17	0.8709(3)	-0.2097(3)	0.0883(3)	4.1(2)
C18	0.8597(3)	-0.2417(3)	0.1133(3)	3.6(2)
C19	0.6431(2)	-0.4628(3)	0.0049(2)	2.9(2)
C20	0.5956(3)	-0.4910(3)	0.0138(3)	3.4(2)
C21	0.5042(3)	-0.5770(3)	-0.0619(3)	4.2(2)
C22	0.4586(3)	-0.6360(3)	-0.1464(3)	4.3(2)
C23	0.5051(3)	-0.6096(3)	-0.1553(3)	4.4(2)
C24	0.5953(3)	-0.5250(3)	-0.0817(3)	3.7(2)
C25	1.0766(3)	-0.1006(3)	0.4741(3)	3.7(2)
C26	1.0504(3)	-0.1733(3)	0.4459(3)	3.5(2)
C27	0.9768(3)	-0.2261(3)	0.4219(3)	3.5(2)
C28	0.9566(3)	-0.1878(3)	0.4334(3)	3.8(2)
C29	1.0192(3)	-0.1092(3)	0.4666(3)	4.0(2)
C30	0.8303(3)	-0.1891(3)	0.3162(3)	4.1(2)
C31	0.7408(3)	-0.2703(3)	0.2275(3)	4.2(2)
C32	0.7346(3)	-0.2666(3)	0.1771(3)	4.2(2)
C33	0.8211(3)	-0.1814(3)	0.2367(3)	3.7(2)
C34	0.8808(3)	-0.1332(3)	0.2249(3)	3.9(2)
C35	0.8098(2)	-0.3258(3)	0.2412(2)	2.7(2)
C36	0.9457(2)	-0.1827(2)	0.3013(2)	2.7(2)
C37	0.8169(2)	-0.4130(3)	0.1271(3)	2.9(2)
C38	0.8105(2)	-0.3798(3)	0.0969(2)	3.0(2)

Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
Fe1'	0.45527(4)	-0.21922(4)	-0.31347(3)	2.61(3)
Fe2'	0.56901(4)	-0.12334(4)	-0.15227(4)	2.93(3)
P1'	0.34943(7)	-0.36083(7)	-0.40100(7)	2.85(5)
P2'	0.52422(7)	-0.21910(7)	-0.16260(7)	2.86(5)
O1'	0.4019(2)	-0.1974(2)	-0.2455(2)	3.8(1)
O2'	0.5900(2)	-0.1959(2)	-0.2419(2)	4.8(2)
C1'	0.3358(3)	-0.4356(3)	-0.4736(3)	3.2(2)
C2'	0.3919(3)	-0.4039(3)	-0.4717(3)	4.3(2)
C3'	0.3780(3)	-0.4616(3)	-0.5302(3)	5.4(3)
C4'	0.3099(3)	-0.5501(3)	-0.5887(3)	6.0(3)
C5'	0.2535(3)	-0.5841(3)	-0.5908(4)	5.8(3)
C6'	0.2658(3)	-0.5284(3)	-0.5343(3)	4.2(2)
C7'	0.2347(3)	-0.4249(3)	-0.4851(2)	2.9(2)
C8'	0.1738(3)	-0.4861(3)	-0.5758(3)	3.8(2)
C9'	0.0905(3)	-0.5278(3)	-0.6357(3)	4.6(3)
C10'	0.0670(3)	-0.5085(3)	-0.6047(3)	5.4(3)
C11'	0.1252(3)	-0.4493(4)	-0.5155(3)	5.7(3)
C12'	0.2076(3)	-0.4079(3)	-0.4559(3)	4.8(3)
C13'	0.6160(3)	-0.1867(3)	-0.0823(3)	3.6(2)
C14'	0.6582(3)	-0.1398(3)	0.0010(3)	4.1(2)
C15'	0.7315(3)	-0.1097(3)	0.0632(3)	5.0(3)
C16'	0.7644(4)	-0.1245(3)	0.0451(4)	6.0(3)
C17'	0.7241(3)	-0.1709(4)	-0.0369(4)	6.8(3)
C18'	0.6504(3)	-0.2018(3)	-0.1008(3)	5.0(2)
C19'	0.4661(3)	-0.2442(3)	-0.1447(3)	3.1(2)
C20'	0.4461(3)	-0.2073(3)	-0.1289(3)	3.5(2)
C21'	0.3977(3)	-0.2306(3)	-0.1204(3)	4.4(2)
C22'	0.3688(3)	-0.2914(3)	-0.1272(3)	4.9(3)
C23'	0.3897(3)	-0.3277(3)	-0.1415(3)	4.9(3)
C24'	0.4370(3)	-0.3051(3)	-0.1508(3)	4.1(2)
C25'	0.4818(3)	-0.1983(3)	-0.3677(3)	4.4(2)
C26'	0.3895(4)	-0.2646(3)	-0.4297(3)	4.9(3)
C27'	0.3795(3)	-0.2246(3)	-0.3905(3)	5.2(2)
C28'	0.4667(3)	-0.1339(3)	-0.3034(3)	4.2(2)
C29'	0.5288(3)	-0.1178(3)	-0.2893(3)	4.0(2)
C30'	0.6462(4)	0.0073(3)	-0.0828(3)	5.0(3)
C31'	0.6255(3)	-0.0045(3)	-0.0485(3)	4.7(2)
C32'	0.6629(3)	-0.0176(3)	-0.0133(3)	4.7(3)
C33'	0.7097(3)	-0.0126(3)	-0.0237(3)	4.9(3)
C34'	0.6978(3)	0.0028(3)	-0.0673(3)	5.5(3)
C35'	0.4514(3)	-0.1881(2)	-0.2394(2)	2.8(2)
C36'	0.5530(3)	-0.1874(3)	-0.2389(3)	3.1(2)
C37'	0.3506(3)	-0.3833(3)	-0.3485(3)	3.3(2)
C38'	0.4421(3)	-0.3357(3)	-0.2724(3)	3.3(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Tables A-9 through A-12

for $(n^5\text{-}C_5H_5)(n^5\text{-}C_5H_4CHO)Fe_2CO_2(u\text{-}DPPM)$, IV

Table A-9: Crystal Data

formula	$C_{38}H_{32}O_3P_2Fe_2$
crystal system	monoclinic
space group	C2/c (No. 15)
a	23.100(5)
b	12.383(1)
c	23.630(4)
α	90
β	111.28(8)
γ	90
Volume Å^3	6299(2)
Z	8
D(calc) g/cm^3	1.523
D(obs) g/cm^3	1.499
u(Mo Kα) cm^{-1}	10.59
temp K	296
crystal size,mm	0.25 x 0.35 x 0.47
crystal color	dk. green
	(ii) Data Collection
diffractometer	Enraf-Nonius CAD4
monochromator	oriented graphite
radiation	Mo Kα
wavelength	0.71073
2θ limits, deg	0.5950
scan technique	θ-2θ
standards	3 std/100 refls
decay (max)	6.8 %
octants collcd	±h, ±k, ±l (1 - 10° 2θ) h, ±k, ±l (10 - 50° 2θ)
no.of rflns collcd	12294
no of independt rflns	5821
no of independt rflns Fo ≥ 3σ(Fc)	3687
R(I) on averaging	1.5%
T(max)/T(min)	1.06
	(iii) Refinement
R(F), %	3.9 %
R_w(F), %	5.8 %
GOF	2.014
Δ/σ	0.01
Δ(ρ), e Å^{-3}	1.50
N_o/N_v	9.5/1

a These structure has not been completely determined. The formyl group is badly disordered and has not been completely modeled. However, the current structure is consistent with only one formyl group per molecule.

Table A-10: Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe1	Fe2	2.526(1)	P2	C37	1.839(5)
Fe1	P1	2.182(1)	O1	C35	1.196(5)
Fe1	C25	2.125(6)	O2	C36	1.188(5)
Fe1	C26	2.096(7)	O3	C38	1.068(0)
Fe1	C27	2.101(7)	C1	C2	1.405(5)
Fe1	C28	2.125(7)	C1	C6	1.376(8)
Fe1	C29	2.135(6)	C2	C3	1.398(9)
Fe1	C35	1.902(4)	C3	C4	1.39(1)
Fe1	C36	1.910(5)	C4	C5	1.373(7)
Fe2	P2	2.192(1)	C5	C6	1.378(8)
Fe2	C30	2.129(6)	C7	C8	1.368(8)
Fe2	C31	2.110(6)	C7	C12	1.397(7)
Fe2	C32	2.100(6)	C8	C9	1.393(7)
Fe2	C33	2.131(5)	C9	C10	1.346(7)
Fe2	C34	2.111(6)	C10	C11	1.395(9)
Fe2	C35	1.906(5)	C11	C12	1.377(8)
Fe2	C36	1.891(4)	C13	C14	1.391(5)
P1	C1	1.833(5)	C13	C18	1.375(7)
P1	C7	1.839(5)	C14	C15	1.374(8)
P1	C37	1.840(4)	C15	C16	1.355(9)
P2	C13	1.838(5)	C16	C17	1.375(7)
P2	C19	1.837(4)	C17	C18	1.380(7)
C19	C20	1.386(6)	C27	C28	1.45(1)
C19	C24	1.389(7)	C28	C29	1.454(8)
C20	C21	1.397(7)	C30	C31	1.422(9)
C21	C22	1.364(9)	C30	C34	1.408(8)
C22	C23	1.351(8)	C30	C38	1.350(6)
C23	C24	1.389(6)	C31	C32	1.390(8)
C25	C26	1.32(1)	C32	C33	1.362(7)
C25	C29	1.36(1)	C33	C34	1.412(9)
C26	C27	1.343(9)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-11: Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Fe2	Fe1	P1	96.13(4)	C26	Fe1	C28	64.8(3)
Fe2	Fe1	C25	131.8(2)	C26	Fe1	C29	62.8(3)
Fe2	Fe1	C26	168.1(2)	C26	Fe1	C35	140.8(2)
Fe2	Fe1	C27	146.8(2)	C26	Fe1	C36	123.1(2)
Fe2	Fe1	C28	112.5(2)	C27	Fe1	C28	40.1(3)
Fe2	Fe1	C29	107.2(2)	C27	Fe1	C29	65.0(2)
Fe2	Fe1	C35	48.5(1)	C27	Fe1	C35	104.7(2)
Fe2	Fe1	C36	48.0(1)	C27	Fe1	C36	154.6(2)
P1	Fe1	C25	115.4(2)	C28	Fe1	C29	39.9(2)
P1	Fe1	C26	92.1(2)	C28	Fe1	C35	91.5(2)
P1	Fe1	C27	102.4(2)	C28	Fe1	C36	126.3(3)
P1	Fe1	C28	140.6(2)	C29	Fe1	C35	118.5(2)
P1	Fe1	C29	152.6(2)	C29	Fe1	C36	92.3(2)
P1	Fe1	C35	87.7(1)	C35	Fe1	C36	96.0(2)
P1	Fe1	C36	92.9(1)	Fe1	Fe2	P2	95.75(4)
C25	Fe1	C26	36.3(3)	Fe1	Fe2	C30	113.7(2)
C25	Fe1	C27	62.4(3)	Fe1	Fe2	C31	148.5(2)
C25	Fe1	C28	64.5(3)	Fe1	Fe2	C32	164.9(1)
C25	Fe1	C29	37.4(3)	Fe1	Fe2	C33	127.4(2)
C25	Fe1	C35	154.8(3)	Fe1	Fe2	C34	104.9(2)
C25	Fe1	C36	92.7(2)	Fe1	Fe2	C35	48.4(1)
C26	Fe1	C27	37.3(2)	Fe1	Fe2	C36	48.7(1)
P2	Fe2	C30	138.8(2)	C33	Fe2	C34	38.9(3)
P2	Fe2	C31	102.4(2)	C33	Fe2	C35	151.8(2)
P2	Fe2	C32	93.4(2)	C33	Fe2	C36	89.5(2)
P2	Fe2	C33	119.0(2)	C34	Fe2	C35	113.1(2)
P2	Fe2	C34	156.9(2)	C34	Fe2	C36	94.2(2)
P2	Fe2	C35	88.4(1)	C35	Fe2	C36	96.5(2)
P2	Fe2	C36	91.6(1)	Fe1	P1	C1	120.9(1)
C30	Fe2	C31	39.2(3)	Fe1	P1	C7	114.6(2)
C30	Fe2	C32	65.2(3)	Fe1	P1	C37	111.5(2)
C30	Fe2	C33	65.1(2)	C1	P1	C7	102.5(2)
C30	Fe2	C34	38.8(2)	C1	P1	C37	101.3(2)
C30	Fe2	C35	90.4(2)	C7	P1	C37	104.0(2)
C30	Fe2	C36	129.4(2)	Fe2	P2	C13	119.4(1)
C31	Fe2	C32	38.6(2)	Fe2	P2	C19	116.9(2)
C31	Fe2	C33	64.0(2)	Fe2	P2	C37	111.0(2)
C31	Fe2	C34	64.6(2)	C13	P2	C19	102.0(2)
C31	Fe2	C35	106.2(2)	C13	P2	C37	103.2(2)
C31	Fe2	C36	153.4(2)	C19	P2	C37	102.1(2)
C32	Fe2	C33	37.5(2)	P1	C1	C2	119.3(4)
C32	Fe2	C34	64.2(3)	P1	C1	C6	121.4(3)
C32	Fe2	C35	144.1(2)	C2	C1	C6	119.2(5)
C32	Fe2	C36	119.2(2)	C1	C2	C3	119.6(5)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C2	C3	C4	119.3(4)	C20	C19	C24	118.4(4)
C3	C4	C5	121.1(6)	C19	C20	C21	120.6(5)
C4	C5	C6	119.2(6)	C20	C21	C22	119.7(5)
C1	C6	C5	121.7(4)	C21	C22	C23	120.3(5)
P1	C7	C8	122.9(3)	C22	C23	C24	121.2(6)
P1	C7	C12	118.4(4)	C19	C24	C23	119.7(4)
C8	C7	C12	118.5(4)	Fe1	C25	C26	70.6(4)
C7	C8	C9	120.5(5)	Fe1	C25	C29	71.7(4)
C8	C9	C10	121.2(6)	C26	C25	C29	110.6(6)
C9	C10	C11	119.2(5)	Fe1	C26	C25	73.0(4)
C10	C11	C12	120.1(5)	Fe1	C26	C27	71.5(4)
C7	C12	C11	120.5(6)	C25	C26	C27	110.9(7)
P2	C13	C14	119.5(4)	Fe1	C27	C26	71.1(4)
P2	C13	C18	121.7(3)	Fe1	C27	C28	70.9(4)
C14	C13	C18	118.8(4)	C26	C27	C28	108.1(5)
C13	C14	C15	120.3(5)	Fe1	C28	C27	69.0(4)
C14	C15	C16	120.1(4)	Fe1	C28	C29	70.4(4)
C15	C16	C17	120.6(5)	C27	C28	C29	103.3(5)
C16	C17	C18	119.6(5)	Fe1	C29	C25	70.9(4)
C13	C18	C17	120.4(4)	Fe1	C29	C28	69.7(3)
P2	C19	C20	118.2(4)	C25	C29	C28	107.1(6)
P2	C19	C24	123.2(3)	Fe2	C30	C31	69.7(4)
Fe2	C30	C34	69.9(4)	C32	C33	C34	107.7(5)
Fe2	C30	C38	121.1(4)	Fe2	C34	C30	71.3(3)
C31	C30	C34	105.6(5)	Fe2	C34	C33	71.4(3)
C31	C30	C38	124.5(5)	C30	C34	C33	108.8(6)
C34	C30	C38	129.7(6)	Fe1	C35	Fe2	83.1(2)
Fe2	C31	C30	71.1(4)	Fe1	C35	O1	139.2(4)
Fe2	C31	C32	70.3(4)	Fe2	C35	O1	137.6(4)
C30	C31	C32	108.3(4)	Fe1	C36	Fe2	83.3(2)
Fe2	C32	C31	71.1(4)	Fe1	C36	O2	137.7(4)
Fe2	C32	C33	72.5(4)	Fe2	C36	O2	137.9(4)
C31	C32	C33	109.5(5)	P1	C37	P2	108.2(2)
Fe2	C33	C32	70.0(3)	O3	C38	C30	119.4(3)
Fe2	C33	C34	69.8(3)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-12: Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Fe1	0.60125(4)	0.05726(8)	0.65236(4)	3.29(2)
Fe2	0.67847(4)	0.04900(7)	0.59937(3)	3.09(2)
P1	0.62988(6)	0.2153(1)	0.69393(6)	3.05(3)
P2	0.71960(6)	0.2061(1)	0.62981(6)	2.79(3)
O1	0.7259(2)	-0.0143(4)	0.7265(2)	4.4(1)
O2	0.5589(2)	0.1398(4)	0.5291(2)	4.6(1)
C1	0.5890(3)	0.3380(6)	0.6580(3)	3.8(1)
C2	0.5371(3)	0.3306(7)	0.6045(3)	4.5(2)
C3	0.5088(3)	0.4251(8)	0.5744(3)	6.2(2)
C4	0.5313(4)	0.5238(8)	0.5986(4)	6.9(2)
C5	0.5815(4)	0.5314(7)	0.6519(4)	6.1(2)
C6	0.6105(3)	0.4394(7)	0.6810(3)	4.9(2)
C7	0.6322(3)	0.2270(6)	0.7720(3)	3.7(1)
C8	0.5939(3)	0.2963(6)	0.7883(3)	4.6(2)
C9	0.5944(3)	0.2977(7)	0.8474(3)	5.5(2)
C10	0.6325(3)	0.2307(7)	0.8899(3)	5.6(2)
C11	0.6699(4)	0.1598(8)	0.8746(3)	5.7(2)
C12	0.6695(3)	0.1581(7)	0.8158(3)	4.9(2)
C13	0.6907(2)	0.3246(5)	0.5803(2)	3.2(1)
C14	0.6575(3)	0.3101(6)	0.5188(3)	3.9(1)
C15	0.6374(3)	0.3985(7)	0.4810(3)	4.9(2)
C16	0.6487(3)	0.5008(6)	0.5039(3)	5.2(2)
C17	0.6801(3)	0.5173(6)	0.5645(4)	5.2(2)
C18	0.7018(3)	0.4304(6)	0.6030(3)	4.3(2)
C19	0.8042(2)	0.2199(5)	0.6497(2)	3.2(1)
C20	0.8418(3)	0.1440(6)	0.6884(3)	4.6(2)
C21	0.9063(3)	0.1478(7)	0.7034(3)	5.5(2)
C22	0.9321(3)	0.2259(8)	0.6796(3)	5.4(2)
C23	0.8956(3)	0.3009(7)	0.6420(3)	5.2(2)
C24	0.8316(3)	0.2986(6)	0.6263(3)	4.1(1)
C25	0.5044(4)	0.0260(9)	0.6206(5)	7.9(3)
C26	0.5236(3)	0.0536(9)	0.6786(4)	7.5(2)
C27	0.5674(4)	-0.0185(8)	0.7131(3)	7.0(2)
C28	0.5768(4)	-0.0988(7)	0.6731(4)	7.6(2)
C29	0.5346(3)	-0.0652(7)	0.6147(4)	7.2(2)
C30	0.7071(4)	-0.1100(6)	0.5889(4)	6.3(2)
C31	0.7512(3)	-0.0343(7)	0.5851(4)	5.9(2)
C32	0.7218(3)	0.0322(6)	0.5354(3)	5.0(2)
C33	0.6610(3)	-0.0007(7)	0.5082(3)	5.3(2)
C34	0.6513(4)	-0.0878(7)	0.5418(3)	6.1(2)
C35	0.6872(3)	0.0184(5)	0.6812(3)	3.4(1)
C36	0.5968(3)	0.1073(5)	0.5745(3)	3.4(1)
C37	0.7102(3)	0.2475(5)	0.7012(2)	3.0(1)
C38	0.720	-0.184	0.635	6.7(6)*
O3	0.684	-0.237	0.636	11.5(8)*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

* These atoms are one member of the disordered formyl groups in the crystal. These positions have been fixed but atoms have been allowed isotropic thermal motion.

Tables A-13 through A-16

for $(n^5\text{-}C_5H_5)(n^5\text{-}C_5H_4CHO)Fe_2CO_2(u\text{-}DPPE)$, V

Table A-13: Crystal Data

formula	$C_{39}H_{34}O_3P_2Fe_2$
crystal system	orthorhombic
space group	
	$Pna2_1$ (No. 33)
a	13.988(10)
b	13.371(3)
c	17.358(6)
α	90
β	90
γ	90
Volume Å^3	3246.5(41)
Z	4
D(calc) g/cm^3	1.481
D(obs) g/cm^3	1.463
u(Mo Kα) cm^{-1}	10.5
temp K	296
crystal size,mm	0.25 x 0.25 x 0.20
crystal color	dark brown
diffractometer	Enraf-Nonius CAD4
monochromator	oriented graphite
radiation	Mo Kα
wavelength	0.71073
2Θ limits, deg	2-50
scan technique	Θ-2Θ
standards	3 std/100 refls
decay (max)	1.6 %
octants collcd	±h,±k,±l (0-24° 2Θ)
	h,k,±l (24-50° 2Θ)
no.of rflns collcd	5360
no of independt rflns	4704
no of independt rflns	
Fo ≥ 3σ (Fo)	3368
R(I) on averaging	1.7%
T(max)/T(min)	1.35
R(F), %	6.9
R_w(F), %	5.8
GOF	1.823
Δ/σ	0.01
Δ(ρ), e Å^{-3}	1.69 near Fe
	0.81 near light atoms
N_o/N_v	8.13

Table A-14: Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Fe1	Fe2	2.527(1)	P2	C19	1.835(8)
Fe1	P1	2.197(2)	O1	C36	1.172(9)
Fe1	C36	1.926(7)	O2	C37	1.185(9)
Fe1	C37	1.916(8)	O3	C35	1.27(2)
Fe1	C25	2.135(8)	C38	C39	1.57(1)
Fe1	C26	2.110(9)	C25	C26	1.43(1)
Fe1	C27	2.127(8)	C25	C29	1.46(1)
Fe1	C28	2.134(9)	C25	C35	1.44(1)
Fe1	C29	2.151(9)	C26	C27	1.41(1)
Fe2	P2	2.188(2)	C27	C28	1.40(2)
Fe2	C36	1.904(8)	C28	C29	1.42(1)
Fe2	C37	1.917(7)	C30	C31	1.42(1)
Fe2	C30	2.139(9)	C30	C34	1.40(1)
Fe2	C31	2.11(1)	C31	C32	1.38(1)
Fe2	C32	2.092(9)	C32	C33	1.40(1)
Fe2	C33	2.113(9)	C33	C34	1.39(1)
Fe2	C34	2.133(9)	C1	C2	1.36(1)
P1	C38	1.798(8)	C1	C6	1.36(1)
P1	C1	1.851(8)	C2	C3	1.37(1)
P1	C7	1.854(8)	C3	C4	1.34(2)
P2	C39	1.838(8)	C4	C5	1.38(1)
P2	C13	1.825(8)	C5	C6	1.37(1)
C7	C8	1.33(1)	C15	C16	1.33(2)
C7	C12	1.39(1)	C16	C17	1.35(2)
C8	C9	1.39(2)	C17	C18	1.42(2)
C9	C10	1.38(2)	C19	C20	1.43(1)
C10	C11	1.34(2)	C19	C24	1.35(1)
C11	C12	1.34(1)	C20	C21	1.38(1)
C13	C14	1.42(1)	C21	C22	1.38(2)
C13	C18	1.38(1)	C22	C23	1.34(2)
C14	C15	1.38(1)	C23	C24	1.39(1)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-15: Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Fe2	Fe1	P1	104.86(7)	C37	Fe1	C26	130.0(3)
Fe2	Fe1	C36	48.3(2)	C37	Fe1	C27	159.7(4)
Fe2	Fe1	C37	48.8(2)	C37	Fe1	C28	127.3(4)
Fe2	Fe1	C25	129.2(2)	C37	Fe1	C29	95.0(3)
Fe2	Fe1	C26	165.9(3)	C25	Fe1	C26	39.4(4)
Fe2	Fe1	C27	136.0(3)	C25	Fe1	C27	64.9(3)
Fe2	Fe1	C28	103.8(3)	C25	Fe1	C28	64.8(3)
Fe2	Fe1	C29	99.2(2)	C25	Fe1	C29	39.8(3)
P1	Fe1	C36	88.0(2)	C26	Fe1	C27	38.9(3)
P1	Fe1	C37	94.7(2)	C26	Fe1	C28	65.1(4)
P1	Fe1	C25	115.6(3)	C26	Fe1	C29	66.7(4)
P1	Fe1	C26	89.2(3)	C27	Fe1	C28	38.3(4)
P1	Fe1	C27	101.2(3)	C27	Fe1	C29	65.4(4)
P1	Fe1	C28	138.0(3)	C28	Fe1	C29	38.8(4)
P1	Fe1	C29	154.6(2)	Fe1	Fe2	P2	106.17(7)
C36	Fe1	C37	94.4(3)	Fe1	Fe2	C36	49.1(2)
C36	Fe1	C25	152.8(3)	Fe1	Fe2	C37	48.7(2)
C36	Fe1	C26	135.5(3)	Fe1	Fe2	C30	100.6(3)
C36	Fe1	C27	98.7(3)	Fe1	Fe2	C31	126.1(3)
C36	Fe1	C28	88.7(3)	Fe1	Fe2	C32	163.9(3)
C36	Fe1	C29	114.6(3)	Fe1	Fe2	C33	141.2(3)
C37	Fe1	C25	96.8(3)	Fe1	Fe2	C34	107.1(3)
P2	Fe2	C36	94.6(2)	C31	Fe2	C32	38.4(4)
P2	Fe2	C37	89.6(2)	C31	Fe2	C33	64.6(4)
P2	Fe2	C30	152.0(3)	C31	Fe2	C34	65.4(4)
P2	Fe2	C31	114.9(3)	C32	Fe2	C33	38.8(4)
P2	Fe2	C32	88.2(3)	C32	Fe2	C34	65.0(4)
P2	Fe2	C33	98.6(3)	C33	Fe2	C34	38.2(4)
P2	Fe2	C34	135.0(3)	Fe1	P1	C38	117.5(3)
C36	Fe2	C37	95.1(3)	Fe1	P1	C1	121.9(3)
C36	Fe2	C30	96.7(4)	Fe1	P1	C7	112.2(3)
C36	Fe2	C31	93.1(4)	C38	P1	C1	98.9(4)
C36	Fe2	C32	124.1(3)	C38	P1	C7	101.5(4)
C36	Fe2	C33	157.3(3)	C1	P1	C7	101.9(4)
C36	Fe2	C34	130.2(3)	Fe2	P2	C39	118.0(3)
C37	Fe2	C30	114.7(4)	Fe2	P2	C13	112.7(3)
C37	Fe2	C31	153.4(4)	Fe2	P2	C19	120.1(3)
C37	Fe2	C32	140.8(4)	C39	P2	C13	101.2(4)
C37	Fe2	C33	103.3(4)	C29	P2	C19	98.6(4)
C37	Fe2	C34	90.3(3)	C13	P2	C19	103.3(4)
C30	Fe2	C31	39.1(4)	Fe1	C36	Fe2	82.6(3)
C30	Fe2	C32	64.3(4)	Fe1	C36	O1	135.5(6)
C30	Fe2	C33	63.7(4)	Fe2	C36	O1	141.0(6)
C30	Fe2	C34	38.3(4)	Fe1	C37	Fe2	82.5(3)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Fe1	C37	O2	138.3(6)	Fe2	C30	C31	69.6(5)
Fe2	C37	O2	138.8(6)	Fe2	C30	C34	70.6(6)
P1	C38	C39	110.5(5)	C31	C30	C34	108.6(9)
P2	C39	C38	110.4(5)	Fe2	C31	C30	71.4(5)
Fe1	C25	C26	69.3(5)	Fe2	C31	C32	69.9(5)
Fe1	C25	C29	70.7(5)	C30	C31	C32	106.7(9)
Fe1	C25	C35	128.0(7)	Fe2	C32	C31	71.7(6)
C26	C25	C29	108.4(7)	Fe2	C32	C33	71.4(5)
C26	C25	C35	123.0(9)	C31	C32	C33	108.7(8)
C29	C25	C35	129(1)	Fe2	C33	C32	69.8(5)
Fe1	C26	C25	71.2(5)	Fe2	C33	C34	71.6(5)
Fe1	C26	C27	71.2(5)	C32	C33	C34	109.0(8)
C25	C26	C27	107.3(8)	Fe2	C34	C30	71.1(5)
Fe1	C27	C26	69.9(5)	Fe2	C34	C33	70.2(5)
Fe1	C27	C28	71.1(5)	C30	C34	C33	106.9(8)
C26	C27	C28	108.9(9)	O3	C35	C25	121.(1)
Fe1	C28	C27	70.6(5)	P1	C1	C2	122.2(7)
Fe1	C28	C29	71.3(5)	P1	C1	C6	121.1(6)
C27	C28	C29	110.1(8)	C2	C1	C6	116.6(8)
Fe1	C29	C25	69.5(5)	C1	C2	C3	122.5(9)
Fe1	C29	C28	70.0(5)	C2	C3	C4	119.2(9)
C25	C29	C28	105.2(8)	C3	C4	C5	120.7(9)
C4	C5	C6	118(1)	C13	C14	C15	121.3(8)
C1	C6	C5	122.6(9)	C14	C15	C16	119(1)
P1	C7	C8	122.6(7)	C15	C16	C17	123.(1)
P1	C7	C12	118.9(6)	C16	C17	C18	120.(1)
C8	C7	C12	118.3(8)	C13	C18	C17	118.2(9)
C7	C8	C9	122.(1)	P2	C19	C20	118.7(6)
C8	C9	C10	117.(1)	P2	C19	C24	122.7(6)
C9	C10	C11	122.(1)	C20	C19	C24	118.5(8)
C10	C11	C12	120.(1)	C19	C20	C21	118.7(9)
C7	C12	C11	121.1(9)	C20	C21	C22	120.5(9)
P2	C13	C14	121.6(6)	C21	C22	C23	121(1)
P2	C13	C18	119.9(6)	C22	C23	C24	119(1)
C14	C13	C18	118.5(8)	C19	C24	C23	122.2(8)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-16: Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Fe1	0.33824(6)	0.63630(7)	0.132	2.89(2)
Fe2	0.45883(6)	0.51502(7)	0.18710(7)	2.80(2)
P1	0.3199(1)	0.5898(1)	0.0116(1)	2.84(3)
P2	0.4800(1)	0.3998(1)	0.0994(1)	2.88(4)
O1	0.5341(3)	0.6717(4)	0.0882(4)	4.3(1)
O2	0.2602(3)	0.4485(4)	0.1896(4)	4.5(1)
O3	0.1036(6)	0.6260(7)	0.2687(6)	10.0(3)
C35	0.4741(5)	0.6240(5)	0.1176(4)	3.1(1)
C36	0.3231(5)	0.5042(6)	0.1734(4)	3.3(1)
C37	0.4062(5)	0.5022(6)	-0.0280(4)	3.0(2)
C38	0.4010(5)	0.4008(6)	0.0151(5)	3.3(2)
C25	0.2154(5)	0.7018(6)	0.1862(5)	4.3(2)
C26	0.2369(6)	0.7501(7)	0.1162(5)	4.9(2)
C27	0.3265(6)	0.7948(6)	0.1215(6)	5.1(2)
C28	0.3630(6)	0.7708(6)	0.1941(6)	5.1(2)
C29	0.2958(6)	0.7116(6)	0.2348(5)	4.2(2)
C30	0.5023(7)	0.5521(7)	0.2891(5)	4.9(2)
C31	0.5816(6)	0.5540(7)	0.2523(5)	5.3(2)
C32	0.5707(6)	0.4501(7)	0.2496(5)	4.3(2)
C33	0.4837(6)	0.4263(7)	0.2859(4)	4.4(2)
C34	0.4421(6)	0.5155(7)	0.3087(5)	4.5(2)
C39	0.1269(8)	0.6553(8)	0.2029(7)	7.1(3)
C1	0.2097(5)	0.5277(5)	-0.0225(4)	3.3(2)
C2	0.1342(6)	0.5104(6)	0.0260(5)	4.2(2)
C3	0.0511(6)	0.4656(7)	-0.0004(6)	5.5(2)
C4	0.0447(6)	0.4372(7)	-0.0736(6)	5.4(2)
C5	0.1196(7)	0.4495( )	-0.1230(6)	5.4(2)
C6	0.2013(6)	0.4964(7)	-0.0968(5)	4.4(2)
C7	0.3299(5)	0.6971(6)	-0.0561(4)	3.5(2)
C8	0.2534(7)	0.7367(7)	-0.0910(6)	5.6(2)
C9	0.2628(8)	0.8200(9)	-0.1382(7)	7.9(3)
C10	0.3515(8)	0.8619(7)	-0.1464(6)	6.9(3)
C11	0.4282(7)	0.8213(7)	-0.1127(6)	6.2(2)
C12	0.4192(6)	0.7409(6)	-0.0668(5)	4.6(2)
C13	0.4604(5)	0.2729(5)	0.1356(5)	3.5(2)
C14	0.5377(6)	0.2116(6)	0.1580(5)	4.7(2)
C15	0.5221(7)	0.1173(7)	0.1874(6)	6.0(2)
C16	0.4332(9)	0.0836(7)	0.1948(6)	6.9(3)
C17	0.3548(7)	0.1413(8)	0.1764(7)	7.0(3)
C18	0.3688(6)	0.2377(7)	0.1454(6)	5.3(2)
C19	0.5944(5)	0.3904(6)	0.0487(4)	3.4(2)
C20	0.6597(5)	0.4718(6)	0.0519(5)	4.1(2)
C21	0.7409(6)	0.4690(8)	0.0072(7)	5.7(2)
C22	0.7611(6)	0.3875(9)	-0.0394(7)	6.4(2)
C23	0.6992(6)	0.3090(7)	-0.0418(5)	5.0(2)
C24	0.6169(6)	0.3104(6)	0.0030(5)	4.3(2)

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Tables A-17 through A-20

for $[(\eta^5\text{-}C_5H_5)Ru(CO)]_2(u\text{-}DPPM)$, VII

Table A-17: Crystal Data

formula	$C_{37}H_{32}O_2P_2Ru_2$
crystal system	monoclinic
space group	C2/c(No. 15)
a	23.747(5)
b	11.908(1)
c	24.099(5)
α	90
β	112.241(7)
γ	90
Volume Å^3	6307(4)
Z	8
D(calc) g/cm^3	1.627
D(obs) g/cm^3	1.640
u(Mo Kα) cm^{-1}	10.714
temp K	296
crystal size,mm	0.30 x 0.35 x 0.50
crystal color	orange
	(ii) Data Collection
diffractometer	Enraf-Nonius CAD4
monochromator	oriented graphite
radiation	Mo Kα
wavelength	0.71073
2Θ limits, deg	2-50
scan technique	Θ-2Θ
standards	3 std/100 refls
decay (max)	11.5 %
octants collcd	±h,±k,±l (0-20° 2Θ) h,k,±l (20-50° 2Θ)
no.of rflns collcd	7508
no of independt rflns	6606
no of independt rflns Fo ≥ 3σ (Fo)	4948
R(I) on averaging	1.0 %
T(max)/T(min)	1.08
	(iii) Refinement
R(F), %	2.5 %
R_w(F), %	5.1 %
GOF	1.207
Δ/σ	0.01
Δ(ρ), e Å^{-3}	0.445
N_o/N_v	12.75

Table A-18: Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ru1	Ru2	2.7036(3)	P2	C13	1.831(2)
Ru1	P1	2.2569(6)	P2	C19	1.837(2)
Ru1	C36	2.015(3)	O2	C36	1.169(3)
Ru1	C35	2.011(2)	O1	C35	1.194(3)
Ru1	C27	2.240(4)	C27	C26	1.392(5)
Ru1	C26	2.213(5)	C27	C28	1.371(6)
Ru1	C25	2.228(4)	C26	C25	1.376(8)
Ru1	C29	2.219(5)	C25	C29	1.272(8)
Ru1	C28	2.273(4)	C29	C28	1.348(6)
Ru2	P2	2.2666(6)	C34	C33	1.383(5)
Ru2	C36	2.025(2)	C34	C30	1.426(5)
Ru2	C35	2.006(3)	C33	C32	1.374(4)
Ru2	C34	2.253(3)	C31	C32	1.414(5)
Ru2	C33	2.279(3)	C31	C30	1.412(6)
Ru2	C31	2.253(4)	C7	C12	1.390(3)
Ru2	C32	2.242(4)	C7	C8	1.386(4)
Ru2	C30	2.260(4)	C12	C11	1.384(4)
P1	P2	3.021(1)	C11	C10	1.358(5)
P1	C37	1.844(3)	C10	C9	1.380(4)
P1	C7	1.833(3)	C9	C8	1.398(4)
P1	C1	1.829(3)	C1	C2	1.370(3)
P2	C37	1.839(3)	C1	C6	1.402(4)
C2	C3	1.393(5)	C16	C15	1.376(5)
C3	C4	1.361(5)	C15	C14	1.389(4)
C4	C5	1.367(4)	C19	C24	1.382(4)
C5	C6	1.383(4)	C19	C20	1.397(4)
C13	C18	1.372(4)	C24	C23	1.381(4)
C13	C14	1.394(3)	C23	C22	1.361(5)
C18	C17	1.386(4)	C22	C21	1.365(5)
C17	C16	1.372(4)	C21	C20	1.385(4)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-19: Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Ru2	Ru1	P1	94.26(2)	C35	Ru1	C26	146.0(1)
Ru2	Ru1	C36	48.14(7)	C35	Ru1	C25	144.0(2)
Ru2	Ru1	C35	47.61(8)	C35	Ru1	C29	110.8(1)
Ru2	Ru1	C27	149.7(1)	C35	Ru1	C28	92.8(1)
Ru2	Ru1	C26	159.8(1)	C27	Ru1	C26	36.4(1)
Ru2	Ru1	C25	123.8(1)	C27	Ru1	C25	59.6(2)
Ru2	Ru1	C29	106.5(1)	C27	Ru1	C29	58.4(2)
Ru2	Ru1	C28	116.8(1)	C27	Ru1	C28	35.4(2)
P1	Ru1	C36	90.20(7)	C26	Ru1	C25	36.1(2)
P1	Ru1	C35	85.73(7)	C26	Ru1	C29	57.9(2)
P1	Ru1	C27	104.5(1)	C26	Ru1	C28	59.2(1)
P1	Ru1	C26	101.0(1)	C25	Ru1	C29	33.2(2)
P1	Ru1	C25	129.4(2)	C25	Ru1	C28	57.8(2)
P1	Ru1	C29	158.9(1)	C29	Ru1	C28	34.9(2)
P1	Ru1	C28	135.9(1)	Ru1	Ru2	P2	93.77(2)
C36	Ru1	C35	94.9(1)	Ru1	Ru2	C36	47.84(7)
C36	Ru1	C27	152.03(9)	Ru1	Ru2	C35	47.79(7)
C36	Ru1	C26	118.1(1)	Ru1	Ru2	C34	105.2(1)
C36	Ru1	C25	92.6(2)	Ru1	Ru2	C33	127.63(9)
C36	Ru1	C29	100.9(1)	Ru1	Ru2	C31	145.9(1)
C36	Ru1	C28	133.7(1)	Ru1	Ru2	C32	162.94(8)
C35	Ru1	C27	109.6(1)	Ru1	Ru2	C30	113.0(1)
P2	Ru2	C36	89.13(7)	C33	Ru2	C31	60.0(1)
P2	Ru2	C35	86.13(7)	C33	Ru2	C32	35.4(1)
P2	Ru2	C34	158.1(1)	C33	Ru2	C30	60.3(1)
P2	Ru2	C33	123.1(1)	C31	Ru2	C32	36.7(1)
P2	Ru2	C31	108.39(9)	C31	Ru2	C30	36.5(2)
P2	Ru2	C32	99.7(1)	C32	Ru2	C30	60.8(2)
P2	Ru2	C30	142.3(1)	Ru1	P1	P2	85.94(2)
C36	Ru2	C35	94.8(1)	Ru1	P1	C37	112.54(8)
C36	Ru2	C34	95.6(1)	Ru1	P1	C7	111.58(9)
C36	Ru2	C33	93.0(1)	Ru1	P1	C1	120.72(7)
C36	Ru2	C31	152.7(1)	P2	P1	C37	34.84(7)
C36	Ru2	C32	121.5(1)	P2	P1	C7	138.40(8)
C36	Ru2	C30	128.5(1)	P2	P1	C1	98.71(9)
C35	Ru2	C34	114.6(1)	C37	P1	C7	105.2(1)
C35	Ru2	C33	149.9(1)	C37	P1	C1	102.1(1)
C35	Ru2	C31	106.8(1)	C7	P1	C1	103.1(1)
C35	Ru2	C32	143.1(1)	Ru2	P2	P1	86.02(2)
C35	Ru2	C30	92.6(1)	Ru2	P2	C37	112.32(8)
C34	Ru2	C33	35.5(1)	Ru2	P2	C13	118.30(7)
C34	Ru2	C31	60.6(1)	Ru2	P2	C19	115.94(9)
C34	Ru2	C32	59.8(1)	P1	P2	C37	34.95(7)
C34	Ru2	C30	36.8(1)	P1	P2	C13	97.51(9)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
P1	P2	C19	136.86(8)	C25	C29	C28	112.3(5)
C37	P2	C13	103.4(1)	Ru1	C28	C27	71.0(2)
C37	P2	C19	102.7(1)	Ru1	C28	C29	70.4(3)
C13	P2	C19	102.2(1)	C27	C28	C29	106.2(3)
Ru1	C36	Ru2	84.02(8)	Ru2	C34	C33	73.2(2)
Ru1	C36	O2	138.1(2)	Ru2	C34	C30	71.8(2)
Ru2	C36	O2	136.8(2)	C33	C34	C30	108.6(3)
Ru1	C35	Ru2	84.60(8)	Ru2	C33	C34	71.2(2)
Ru1	C35	O1	137.6(2)	Ru2	C33	C32	70.8(2)
Ru2	C35	O1	137.5(2)	C34	C33	C32	108.7(3)
P1	C37	P2	110.2(1)	Ru2	C31	C32	71.2(2)
Ru1	C27	C26	70.7(3)	Ru2	C31	C30	72.0(2)
Ru1	C27	C28	73.6(3)	C32	C31	C30	107.4(3)
C26	C27	C28	106.6(3)	Ru2	C32	C33	73.8(2)
Ru1	C26	C27	72.8(2)	Ru2	C32	C31	72.1(2)
Ru1	C26	C25	72.5(3)	C33	C32	C31	108.8(3)
C27	C26	C25	106.6(4)	Ru2	C30	C34	71.3(2)
Ru1	C25	C26	71.4(2)	Ru2	C30	C31	71.5(2)
Ru1	C25	C29	73.0(3)	C34	C30	C31	106.5(3)
C26	C25	C29	108.2(4)	P1	C7	C12	119.4(2)
Ru1	C29	C25	73.7(3)	P1	C7	C8	122.1(2)
Ru1	C29	C28	74.7(2)	C12	C7	C8	117.9(3)
C7	C12	C11	120.6(3)	C18	C13	C14	118.9(2)
C12	C11	C10	121.3(3)	C13	C18	C17	121.0(3)
C11	C10	C9	119.5(3)	C18	C17	C16	119.9(3)
C10	C9	C8	119.9(3)	C17	C16	C15	120.1(3)
C7	C8	C9	120.9(2)	C16	C15	C14	120.0(3)
P1	C1	C2	120.6(2)	C13	C14	C15	120.1(3)
P1	C1	C6	120.2(2)	P2	C19	C24	124.2(2)
C2	C1	C6	119.1(3)	P2	C19	C20	117.8(2)
C1	C2	C3	120.1(3)	C24	C19	C20	118.0(2)
C2	C3	C4	120.6(3)	C19	C24	C23	120.7(3)
C3	C4	C5	120.0(3)	C24	C23	C22	120.9(3)
C4	C5	C6	120.6(3)	C23	C22	C21	119.4(3)
C1	C6	C5	119.6(2)	C22	C21	C20	120.8(3)
P2	C13	C18	122.9(2)	C19	C20	C21	120.1(3)
P2	C13	C14	118.2(2)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-20: Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Ru1	0.59703(1)	0.06378(2)	0.65075(1)	2.365(4)
Ru2	0.67629(1)	0.04717(2)	0.59493(1)	2.395(4)
P1	0.63150(2)	0.23327(5)	0.69133(2)	2.23(1)
P2	0.71901(2)	0.21705(5)	0.62765(2)	2.18(1)
O2	0.55697(8)	0.1568(2)	0.52656(8)	3.67(4)
O1	0.72309(9)	-0.0164(2)	0.72485(9)	4.04(5)
C36	0.5931(1)	0.1188(2)	0.5703(1)	2.62(5)
C35	0.6852(1)	0.0192(2)	0.6799(1)	2.74(5)
C37	0.7098(1)	0.2612(2)	0.6969(1)	2.36(4)
C27	0.5545(2)	-0.0105(4)	0.7109(1)	5.65(7)
C26	0.5110(2)	0.0519(3)	0.6661(2)	9.3(1)
C25	0.5021(2)	-0.0015(6)	0.6127(2)	13.0(1)
C29	0.5373(2)	-0.0862(4)	0.6239(2)	12.4(1)
C28	0.5697(2)	-0.0990(3)	0.6830(2)	7.21(9)
C34	0.6449(2)	-0.1028(3)	0.5339(2)	5.61(8)
C33	0.6576(2)	-0.0186(3)	0.5008(1)	4.75(7)
C31	0.7456(2)	-0.0617(3)	0.5778(2)	6.03(9)
C32	0.7181(1)	0.0093(3)	0.5278(1)	4.85(7)
C30	0.6998(2)	-0.1324(3)	0.5822(2)	6.8(1)
C7	0.6345(1)	0.2437(2)	0.7683(1)	2.75(5)
C12	0.6712(1)	0.1701(3)	0.8116(1)	3.78(6)
C11	0.6686(1)	0.1666(3)	0.8680(1)	4.25(7)
C10	0.6303(1)	0.2342(3)	0.8826(1)	4.40(7)
C9	0.5926(1)	0.3070(3)	0.8402(1)	4.53(7)
C8	0.5948(1)	0.3115(3)	0.7831(1)	3.70(6)
C1	0.5919(1)	0.3620(2)	0.6563(1)	2.83(5)
C2	0.5396(1)	0.3573(3)	0.6060(1)	3.74(6)
C3	0.5114(2)	0.4561(3)	0.5782(2)	5.32(8)
C4	0.5347(2)	0.5580(3)	0.6011(2)	5.54(9)
C5	0.5865(2)	0.5640(3)	0.6517(2)	5.09(8)
C6	0.6159(1)	0.4672(3)	0.6797(1)	3.82(6)
C13	0.6915(1)	0.3383(2)	0.5780(1)	2.57(5)
C18	0.7002(1)	0.4471(2)	0.5982(1)	3.55(6)
C17	0.6793(1)	0.5364(3)	0.5588(2)	4.50(7)
C16	0.6494(1)	0.5166(3)	0.4987(1)	4.83(7)
C15	0.6297(1)	0.4081(3)	0.4774(1)	4.26(7)
C14	0.6603(1)	0.3185(3)	0.5169(1)	3.35(6)
C19	0.8017(1)	0.2260(2)	0.6482(1)	2.70(5)
C24	0.8304(1)	0.3110(3)	0.6299(1)	3.71(6)
C23	0.8927(1)	0.3101(3)	0.6459(1)	4.61(7)
C22	0.9273(1)	0.2256(3)	0.6799(1)	4.18(7)
C21	0.9001(1)	0.1416(3)	0.6992(1)	4.82(7)
C20	0.8376(1)	0.1297(3)	0.6832(1)	4.09(6)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Tables A-21 through A-24

for (n^5-C_5H_5)Ru(Cl)DPPM, IX

Table A-21: Crystal Data

formula	$C_{31}H_{29}P_2ClRu$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
a	15.592(4)
b	10.796(2)
c	19.676(6)
α	90
β	109.01(1)
γ	90
Volume Å^3	3131(1)
Z	4
D(calc) g/cm^3	1.530
D(obs) g/cm^3	1.515
u(Mo Kα) cm^{-1}	7.107
temp K	296
crystal size,mm	0.50 x 0.38 x 0.45
crystal color	orange

(ii) Data Collection

diffractometer	Enraf-Nonius CAD4
monochromator	oriented graphite
radiation	Mo Kα
wavelength	0.71073
2θ limits, deg	2-55
scan technique	θ-2θ
standards	3 std/100 refls
decay (max)	7.3 %
octants collcd	±h,±k,±l (0-20° 2θ) h,k,±l (20-55° 2θ)
no.of rflns collcd	8480
no of independt rflns	7185
no of independt rflns Fo ≥ 3σ (Fo)	5256
R(I) on averaging	0.90 %
T(max)/T(min)	1.02

(iii) Refinement

R(F), %	3.1 %
R_w(F), %	4.1 %
GOF	1.655
Δ/σ	0.01
Δ(ρ), e Å^{-3}	0.558
N_o/N_v	15/1

Table A-22: Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ru	Cl	2.431(1)	C8	C9	1.377(8)
Ru	P1	2.273(1)	C9	C10	1.392(8)
Ru	P2	2.284(1)	C10	C11	1.35(1)
Ru	C25	2.164(6)	C11	C12	1.377(9)
Ru	C26	2.155(6)	C13	C14	1.387(7)
Ru	C27	2.206(7)	C13	C18	1.390(7)
Ru	C28	2.212(6)	C14	C15	1.388(8)
Ru	C29	2.235(5)	C15	C16	1.347(9)
P1	C1	1.819(4)	C16	C17	1.382(9)
P1	C7	1.819(4)	C17	C18	1.363(8)
P1	C30	1.846(4)	C19	C20	1.373(7)
P2	C13	1.832(5)	C19	C24	1.383(6)
P2	C19	1.820(5)	C20	C21	1.390(9)
P2	C30	1.843(4)	C21	C22	1.375(9)
C1	C2	1.383(7)	C22	C23	1.364(7)
C1	C6	1.384(6)	C23	C24	1.385(7)
C2	C3	1.389(8)	C25	C26	1.40(1)
C3	C4	1.383(8)	C25	C29	1.374(6)
C4	C5	1.33(1)	C26	C27	1.38(1)
C5	C6	1.408(8)	C27	C28	1.33(1)
C7	C8	1.385(7)	C28	C29	1.43(1)
C7	C12	1.392(7)			

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-23: Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl	Ru	P1	92.88(4)	C26	Ru	C27	37.0(3)
Cl	Ru	P2	90.55(4)	C26	Ru	C28	60.3(2)
Cl	Ru	C25	139.0(2)	C26	Ru	C29	62.1(2)
Cl	Ru	C26	150.1(2)	C27	Ru	C28	34.9(3)
Cl	Ru	C27	113.6(2)	C27	Ru	C29	61.4(2)
Cl	Ru	C28	91.9(2)	C28	Ru	C29	37.4(2)
Cl	Ru	C29	103.4(2)	Ru	P1	C1	117.0(1)
P1	Ru	P2	71.99(4)	Ru	P1	C7	125.9(1)
P1	Ru	C25	128.1(2)	Ru	P1	C30	97.4(1)
P1	Ru	C26	99.7(2)	C1	P1	C7	100.6(2)
P1	Ru	C27	104.8(2)	C1	P1	C30	109.6(2)
P1	Ru	C28	135.6(2)	C7	P1	C30	105.2(2)
P1	Ru	C29	161.8(2)	Ru	P2	C13	120.7(2)
P2	Ru	C25	100.9(2)	Ru	P2	C19	121.5(1)
P2	Ru	C26	119.0(2)	Ru	P2	C30	97.1(1)
P2	Ru	C27	155.9(2)	C13	P2	C19	103.0(2)
P2	Ru	C28	152.1(2)	C13	P2	C30	105.6(2)
P2	Ru	C29	115.2(2)	C19	P2	C30	107.1(2)
C25	Ru	C26	37.7(3)	P1	C1	C2	116.4(3)
C25	Ru	C27	61.6(3)	P1	C1	C6	124.7(4)
C25	Ru	C28	60.7(2)	C2	C1	C6	118.9(4)
C25	Ru	C29	36.4(2)	C1	C2	C3	120.5(5)
C2	C3	C4	120.4(5)	C20	C19	C24	119.1(4)
C3	C4	C5	119.0(5)	C19	C20	C21	121.0(5)
C4	C5	C6	122.3(5)	C20	C21	C22	118.8(5)
C1	C6	C5	118.9(5)	C21	C22	C23	120.8(5)
P1	C7	C8	120.8(3)	C22	C23	C24	120.0(5)
P1	C7	C12	120.4(4)	C19	C24	C23	120.1(4)
C8	C7	C12	118.8(4)	Ru	C25	C26	70.8(4)
C7	C8	C9	120.9(4)	Ru	C25	C29	74.6(4)
C8	C9	C10	119.7(5)	C26	C25	C29	109.7(6)
C9	C10	C11	119.1(6)	Ru	C26	C25	71.5(4)
C10	C11	C12	122.2(6)	Ru	C26	C27	73.5(4)
C7	C12	C11	119.2(5)	C25	C26	C27	107.2(6)
P2	C13	C14	123.0(4)	Ru	C27	C26	69.5(4)
P2	C13	C18	119.2(4)	Ru	C27	C28	72.8(4)
C14	C13	C18	117.8(4)	C26	C27	C28	108.1(7)
C13	C14	C15	120.6(5)	Ru	C28	C27	72.3(4)
C14	C15	C16	120.7(5)	Ru	C28	C29	72.1(3)
C15	C16	C17	119.3(6)	C27	C28	C29	110.9(6)
C16	C17	C18	121.0(6)	Ru	C29	C25	69.0(3)
C13	C18	C17	120.6(5)	Ru	C29	C28	70.4(3)
P2	C19	C20	117.3(4)	C25	C29	C28	104.1(6)
P2	C19	C24	123.5(3)	P1	C30	P2	93.1(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-24: Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Ru	0.15191(3)	0.13142(3)	0.39457(1)	2.986(6)
Cl	0.2048(1)	0.1699(1)	0.49502(5)	4.30(2)
P1	0.29684(8)	0.23120(9)	0.34595(5)	2.79(2)
P2	0.29332(8)	0.00296(9)	0.37374(5)	2.87(2)
C1	0.2857(4)	0.2839(4)	0.2692(2)	3.36(8)
C2	0.2209(5)	0.3814(5)	0.2649(2)	4.4(1)
C3	0.2042(5)	0.4252(5)	0.2081(3)	5.5(1)
C4	0.2509(6)	0.3707(6)	0.1550(2)	6.4(1)
C5	0.3139(6)	0.2772(6)	0.1593(2)	6.1(1)
C6	0.3343(5)	0.2314(5)	0.2160(2)	4.8(1)
C7	0.3642(4)	0.3551(3)	0.3767(2)	3.23(8)
C8	0.4680(4)	0.3867(4)	0.3516(2)	3.86(9)
C9	0.5195(5)	0.4818(5)	0.3753(3)	5.0(1)
C10	0.4652(6)	0.5457(5)	0.4237(3)	6.2(1)
C11	0.3630(6)	0.5144(6)	0.4469(3)	7.0(2)
C12	0.3119(5)	0.4183(5)	0.4260(2)	4.9(1)
C13	0.2910(4)	-0.1091(4)	0.3145(2)	3.47(8)
C14	0.3300(5)	-0.2218(4)	0.3204(3)	4.7(1)
C15	0.3245(6)	-0.3040(5)	0.2745(3)	5.6(1)
C16	0.2831(6)	-0.2752(5)	0.2230(3)	6.0(1)
C17	0.2453(6)	-0.1627(6)	0.2162(3)	5.7(1)
C18	0.2491(4)	-0.0810(5)	0.2609(2)	4.4(1)
C19	0.3494(4)	-0.0752(4)	0.4344(2)	3.39(8)
C20	0.2768(4)	-0.1196(5)	0.4811(2)	4.6(1)
C21	0.3126(6)	-0.1827(6)	0.5286(3)	5.8(1)
C22	0.4227(5)	-0.2000(5)	0.5282(2)	5.2(1)
C23	0.4960(4)	-0.1547(5)	0.4827(2)	4.8(1)
C24	0.4597(4)	-0.0926(4)	0.4352(2)	3.99(9)
C25	0.0250(4)	0.0409(6)	0.3545(3)	6.2(1)
C26	0.0386(5)	0.1527(7)	0.3290(3)	7.4(2)
C27	0.0080(5)	0.2321(6)	0.3754(4)	7.4(2)
C28	-0.0208(4)	0.1726(7)	0.4266(3)	6.6(2)
C29	-0.0127(4)	0.0495(6)	0.4157(3)	5.2(1)
C30	0.3966(4)	0.1104(4)	0.3421(2)	3.34(8)
C31	0.0414(7)	0.1540(7)	0.0988(4)	7.5(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Tables A-25 through A-28

for $(n^5\text{-}C_5H_5)Ru(Cl)DPPE$, **X**

Table A-25: Crystal Data

formula	$C_{31}H_{29}P_2ClRu$
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
a	15.592(4)
b	10.796(2)
c	19.676(6)
α	90
β	109.01(1)
γ	90
Volume Å^3	3131(1)
Z	4
D(calc) g/cm^3	1.530
D(obs) g/cm^3	1.515
u(Mo Kα) cm^{-1}	7.107
temp K	296
crystal size, mm	0.50 x 0.38 x 0.45
crystal color	orange
	(ii) Data Collection
diffractometer	Enraf-Nonius CAD4
monochromator	oriented graphite
radiation	Mo Kα
wavelength	0.71073
2θ limits, deg	2-55
scan technique	θ-2θ
standards	3 std/100 refls
decay (max)	7.3 %
octants collcd	±h,±k,±l (0-10° 2θ) h,k,±l (20-55° 2θ)
no.of rflns collcd	8480
no of independt rflns	7185
no of independt rflns Fo ≥ 3σ (Fo)	5256
R(I) on averaging	0.90 %
T(max)/T(min)	1.02
	(iii) Refinement
R(F), %	3.1 %
R_w(F), %	4.1 %
GOF	1.655
Δ/σ	0.01
Δ(ρ), e Å^{-3}	0.558
N_o/N_v	15/1

Table A-26: Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ru	Cl	2.446(1)	C1	C6	1.390(5)
Ru	P1	2.270(1)	C2	C3	1.379(6)
Ru	P2	2.286(1)	C3	C4	1.380(7)
Ru	C25	2.163(5)	C4	C5	1.364(7)
Ru	C26	2.169(5)	C5	C6	1.374(6)
Ru	C27	2.222(5)	C7	C8	1.374(7)
Ru	C28	2.227(5)	C7	C12	1.387(8)
Ru	C29	2.221(5)	C8	C9	1.392(8)
P1	P2	3.034(1)	C9	C10	1.35(1)
P1	C31	1.838(4)	C10	C11	1.374(9)
P1	C1	1.834(4)	C11	C12	1.371(8)
P1	C7	1.823(4)	C13	C14	1.387(5)
P2	C30	1.849(4)	C13	C18	1.380(6)
P2	C13	1.838(4)	C14	C15	1.385(7)
P2	C19	1.833(4)	C15	C16	1.366(7)
C31	C30	1.521(6)	C16	C17	1.375(6)
C25	C26	1.400(6)	C17	C18	1.378(6)
C25	C29	1.419(6)	C19	C20	1.375(6)
C26	C27	1.405(7)	C19	C24	1.394(6)
C27	C28	1.398(6)	C20	C21	1.383(6)
C28	C29	1.390(8)	C21	C22	1.358(8)
C1	C2	1.380(6)	C22	C23	1.379(6)
C23	C24	1.378(6)	C37	C13	1.723(5)
C37	C12	1.730(6)	C37	C14	1.714(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-27: Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl	Ru	P1	83.01(4)	C26	Ru	C27	37.3(2)
Cl	Ru	P2	93.30(4)	C26	Ru	C28	61.6(2)
Cl	Ru	C25	154.5(1)	C26	Ru	C29	62.4(2)
Cl	Ru	C26	136.1(1)	C27	Ru	C28	36.6(2)
Cl	Ru	C27	101.0(1)	C27	Ru	C29	61.8(2)
Cl	Ru	C28	93.1(1)	C28	Ru	C29	36.4(2)
Cl	Ru	C29	118.3(1)	Ru	P1	P2	48.48(3)
P1	Ru	P2	83.50(4)	Ru	P1	C31	108.3(1)
P1	Ru	C25	120.5(1)	Ru	P1	C1	120.7(1)
P1	Ru	C26	99.6(1)	Ru	P1	C7	117.3(1)
P1	Ru	C27	112.2(1)	P2	P1	C31	63.2(1)
P1	Ru	C28	147.4(1)	P2	P1	C1	113.1(1)
P1	Ru	C29	158.2(1)	P2	P1	C7	146.4(1)
P2	Ru	C25	98.8(1)	C31	P1	C1	101.9(2)
P2	Ru	C26	130.6(1)	C31	P1	C7	106.8(2)
P2	Ru	C27	159.7(1)	C1	P1	C7	100.2(2)
P2	Ru	C28	129.1(1)	Ru	P2	P1	48.01(3)
P2	Ru	C29	98.8(1)	Ru	P2	C30	109.8(1)
C25	Ru	C26	37.7(2)	Ru	P2	C13	116.4(1)
C25	Ru	C27	62.6(2)	Ru	P2	C19	119.8(1)
C25	Ru	C28	61.9(2)	P1	P2	C30	61.8(1)
C25	Ru	C29	37.7(2)	P1	P2	C13	129.0(1)
P1	P2	C19	129.1(1)	P1	C1	C6	120.8(3)
C30	P2	C13	103.8(2)	C2	C1	C6	117.7(3)
C30	P2	C19	104.0(2)	C1	C2	C3	121.5(4)
C13	P2	C19	101.4(2)	C2	C3	C4	119.5(4)
P1	C31	C30	106.9(3)	C3	C4	C5	119.8(4)
P2	C30	C31	108.8(3)	C4	C5	C6	120.5(4)
Ru	C25	C26	71.4(3)	C1	C6	C5	120.9(4)
Ru	C25	C29	73.3(3)	P1	C7	C8	125.2(4)
C26	C25	C29	107.6(4)	P1	C7	C12	116.9(4)
Ru	C26	C25	70.9(3)	C8	C7	C12	117.9(4)
Ru	C26	C27	73.4(3)	C7	C8	C9	120.3(6)
C25	C26	C27	108.7(4)	C8	C9	C10	120.8(6)
Ru	C27	C26	69.3(3)	C9	C10	C11	119.8(5)
Ru	C27	C28	71.9(3)	C10	C11	C12	119.8(6)
C26	C27	C28	106.9(4)	C7	C12	C11	121.5(6)
Ru	C28	C27	71.5(3)	P2	C13	C14	120.8(3)
Ru	C28	C29	71.5(3)	P2	C13	C18	121.0(3)
C27	C28	C29	109.7(5)	C14	C13	C18	118.0(4)
Ru	C29	C25	68.9(3)	C13	C14	C15	120.5(4)
Ru	C29	C28	72.0(3)	C14	C15	C16	120.8(4)
C25	C29	C28	107.1(4)	C15	C16	C17	119.1(5)
P1	C1	C2	121.5(3)	C16	C17	C18	120.4(4)
C13	C18	C17	121.1(4)	C21	C22	C23	119.4(4)
P2	C19	C20	119.8(3)	C22	C23	C24	120.8(5)
P2	C19	C24	121.2(3)	C19	C24	C23	119.6(5)
C20	C19	C24	118.9(4)	C12	C37	C13	110.6(4)
C19	C20	C21	120.5(5)	C12	C37	C14	110.3(3)
C20	C21	C22	120.7(5)	C13	C37	C14	110.3(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table A-28: Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
Ru	0.78207(2)	0.07156(3)	0.82430(2)	2.998(6)
Cl	0.82928(7)	0.28479(9)	0.81380(6)	4.35(2)
P1	0.73875(6)	0.07751(9)	0.70248(5)	3.05(2)
P2	0.91254(6)	-0.01071(9)	0.81427(5)	3.08(2)
C31	0.8413(2)	0.0753(4)	0.6758(2)	3.77(8)
C30	0.9015(3)	-0.0279(4)	0.7183(2)	3.87(9)
C25	0.7421(3)	-0.0813(4)	0.8785(2)	4.9(1)
C26	0.6640(3)	-0.0182(5)	0.8375(2)	4.9(1)
C27	0.6665(3)	0.1025(5)	0.8649(3)	5.5(1)
C28	0.7469(4)	0.1124(5)	0.9230(2)	5.9(1)
C29	0.7936(4)	0.0006(6)	0.9329(2)	5.7(1)
C1	0.6719(2)	-0.0490(4)	0.6482(2)	3.22(7)
C2	0.6617(3)	-0.1607(4)	0.6788(2)	3.77(8)
C3	0.6117(3)	-0.2561(4)	0.6380(3)	4.8(1)
C4	0.5708(3)	-0.2399(5)	0.5650(3)	5.0(1)
C5	0.5808(3)	-0.1304(5)	0.5338(2)	4.8(1)
C6	0.6304(3)	-0.0355(4)	0.5745(2)	4.12(9)
C7	0.6716(3)	0.2103(4)	0.6578(2)	3.77(9)
C8	0.6951(3)	0.2907(5)	0.6126(3)	5.8(1)
C9	0.6380(4)	0.3885(5)	0.5808(3)	7.5(2)
C10	0.5589(5)	0.4062(5)	0.5935(3)	7.3(2)
C11	0.5338(4)	0.3262(6)	0.6380(3)	7.5(1)
C12	0.5895(4)	0.2294(5)	0.6694(3)	6.0(1)
C13	0.9430(3)	-0.1671(4)	0.8513(2)	3.44(8)
C14	1.0095(3)	-0.1843(4)	0.9174(3)	4.9(1)
C15	1.0287(4)	-0.3017(5)	0.9467(3)	5.7(1)
C16	0.9821(3)	-0.4026(5)	0.9115(3)	5.6(1)
C17	0.9152(3)	-0.3862(4)	0.8464(3)	5.4(1)
C18	0.8958(3)	-0.2697(4)	0.8168(2)	4.4(1)
C19	1.0203(2)	0.0716(4)	0.8530(2)	3.49(8)
C20	1.0269(3)	0.1654(4)	0.9018(2)	4.3(1)
C21	1.1082(3)	0.2270(5)	0.9324(3)	5.2(1)
C22	1.1824(3)	0.1975(5)	0.9140(3)	5.6(1)
C23	1.1770(3)	0.1025(5)	0.8659(3)	5.5(1)
C24	1.0969(3)	0.0292(5)	0.8352(2)	4.5(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:
(4/3) * [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

Appendix B:

Infrared Spectral Data

Table B-1. Infrared Spectra in the C≡O and C=O Stretching Regions, in cm^{-1}

Compound[a]	Terminal (C≡O)	Bridging (C=O)	Formyl (C=O)
I. FeDPPM	----	1670	----
II. FeDPPE	----	1671	----
III. FeDPPP	----	1666	----
IV. FeDPPM Photo	----	1690, 1682	1638
V. FeDPPE Photo	----	1687	1655
VI. FeDPPP Photo	1967	----	----
VII. RuDPPM	----	1688	----
VIII. RuDPPM Photo	----	1681	1652

[a]Spectra recorded in $CHCl_3$.

Appendix C:

^{1}H and ^{13}C NMR Spectra in $CDCl_3$

for Selected Compounds

Figure C-1

^1H NMR Spectrum of $[(n^5\text{-}C_5H_5)Fe(CO)]_2(u\text{-}DPPM)$, I

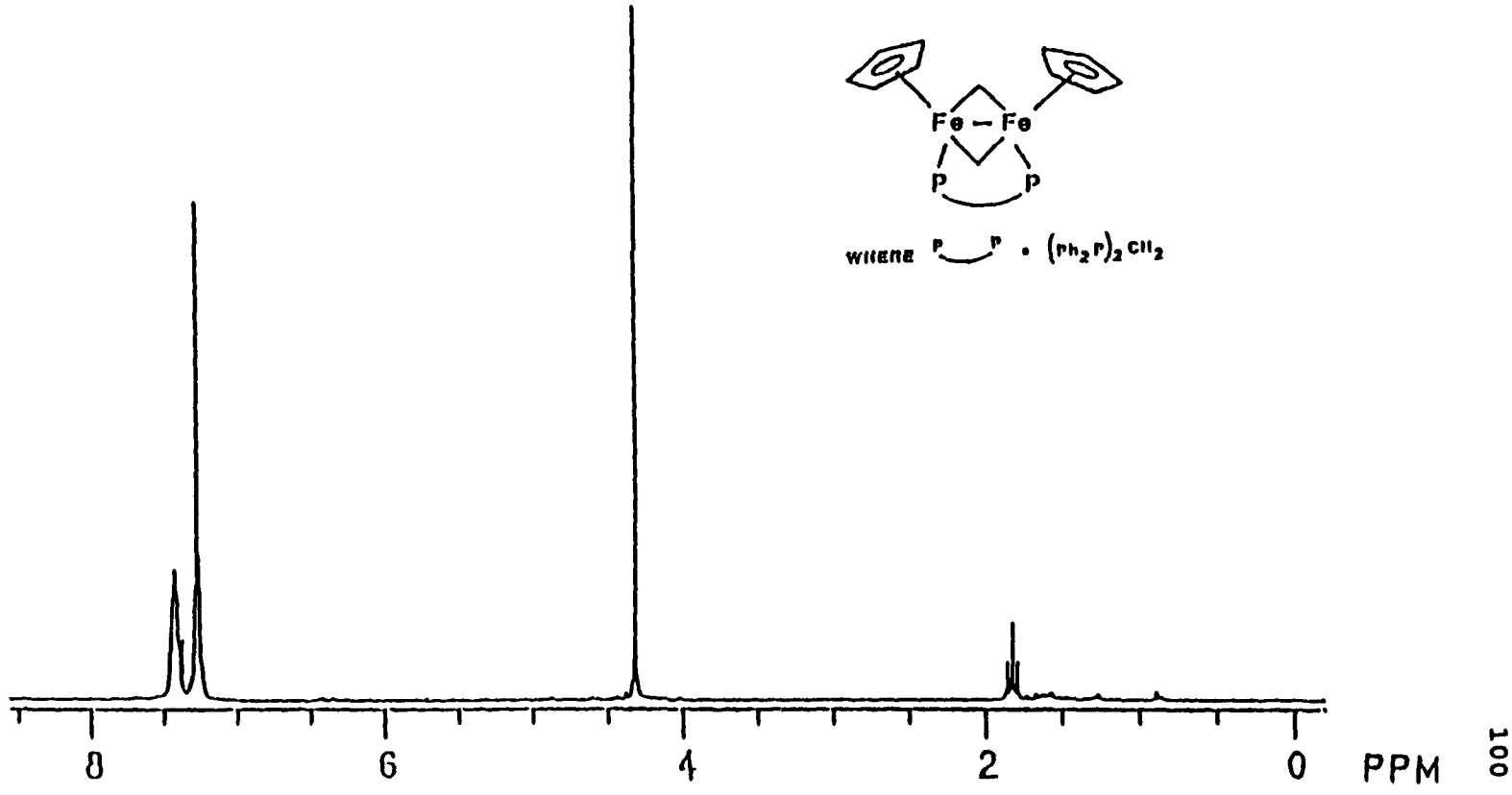

Fe — Fe
P
P
where P⌒P = (Ph2P)2CH2
8
6
4
2
0
PPM

Figure C-2

^{13}C NMR Spectrum of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_2(u\text{-}DPPM)$, I

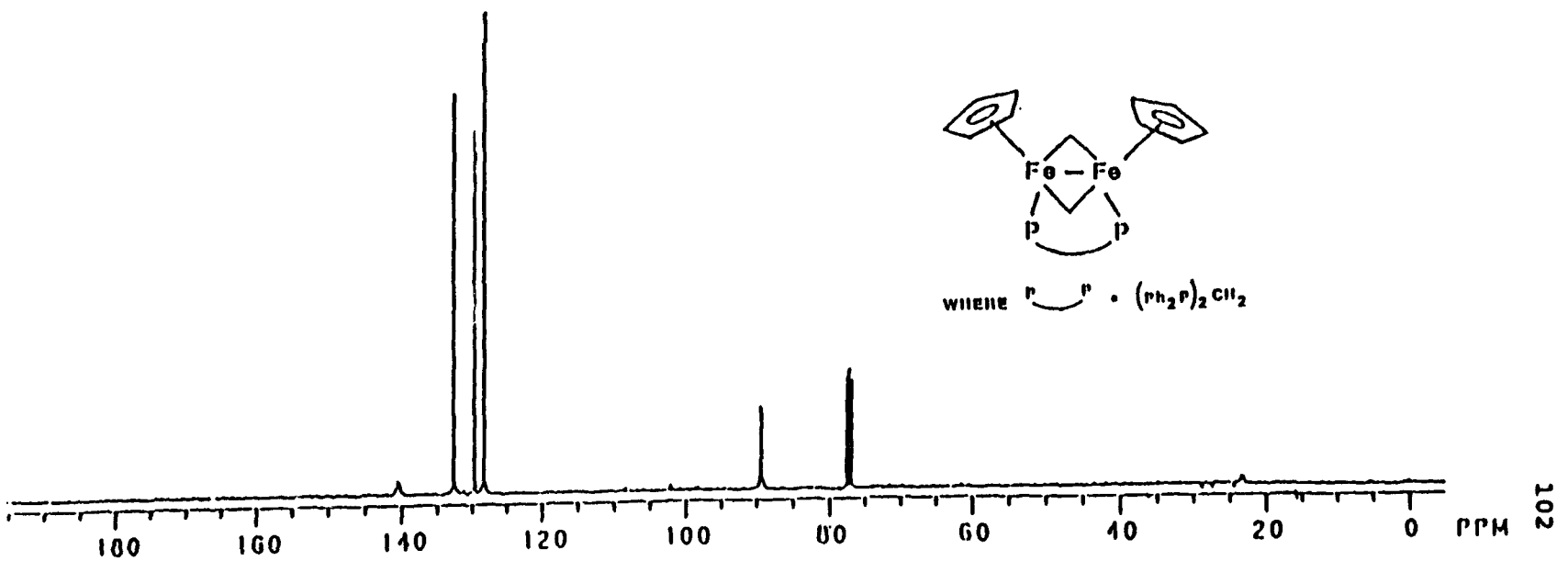

Fe — Fe
P
P
WHERE P⌒P = (Ph2P)2CH2
180
160
140
120
100
80
60
40
20
0
PPM

Figure C-3

^1H NMR Spectrum of $[(n^5\text{-}C_5H_5)Fe(CO)]_2(u\text{-}DPPE)$, II

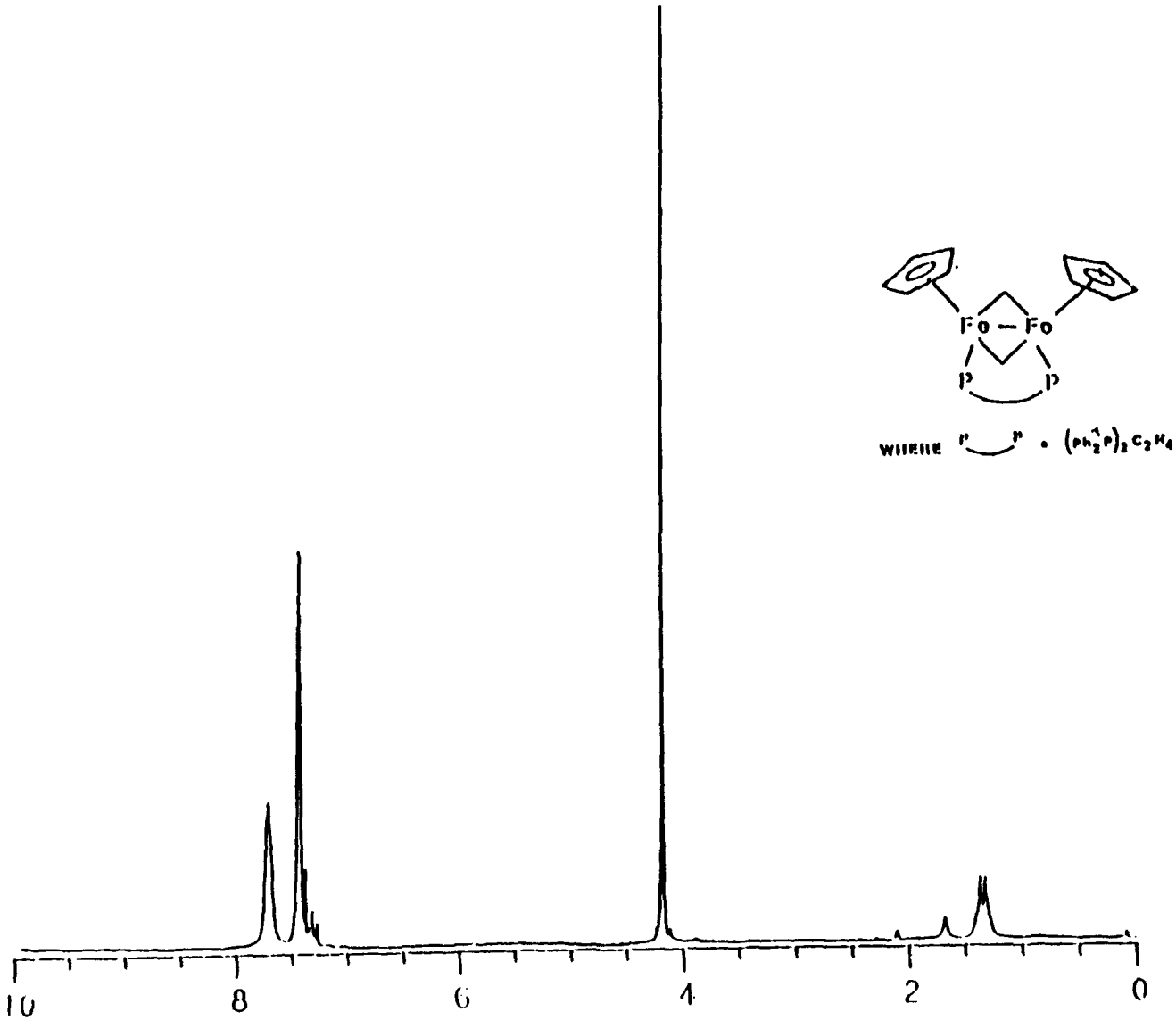
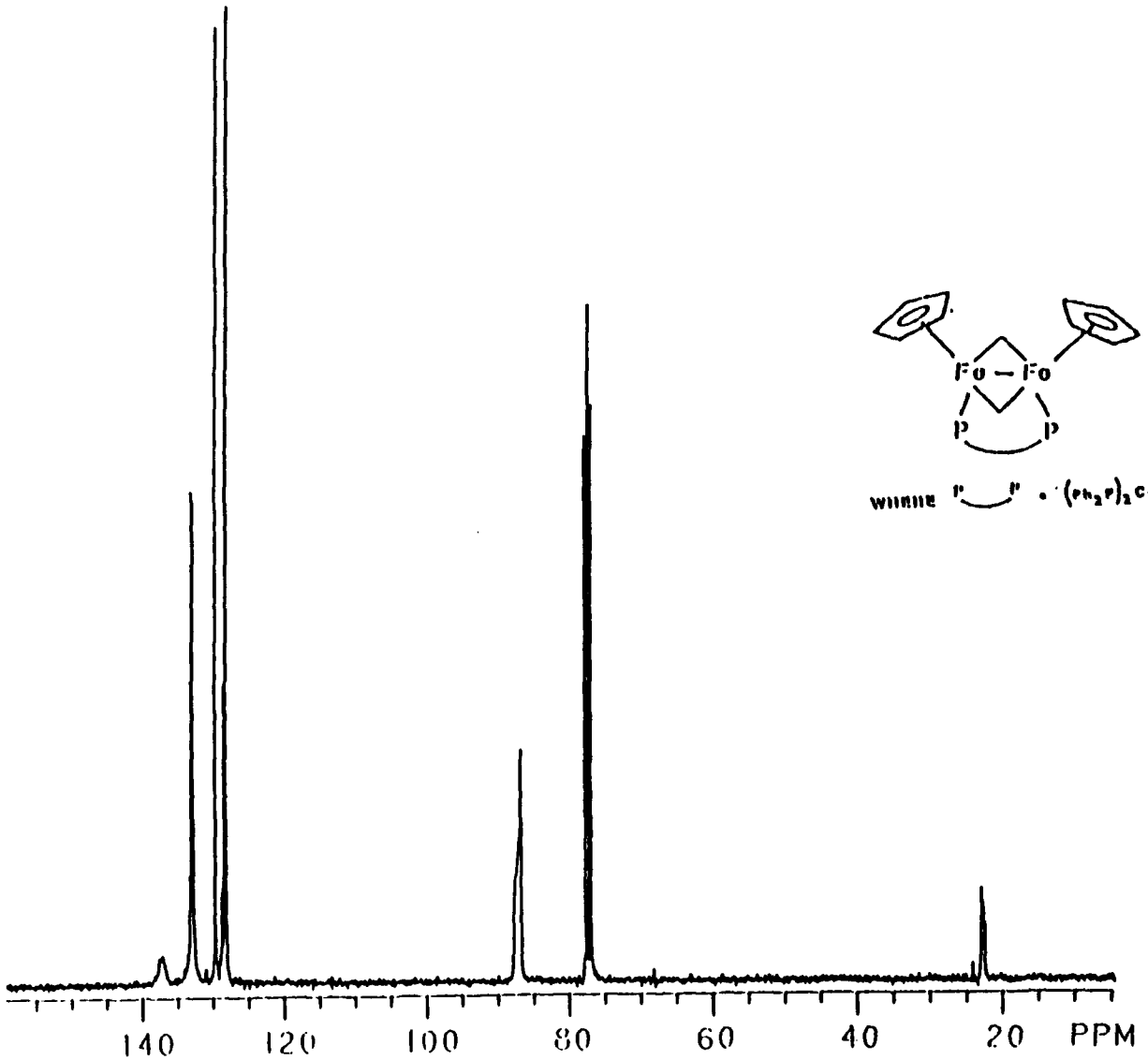

Fe — Fe
P
P
WHERE P—P = $(PH_2^1P)_2C_2H_4$
10
8
6
4
2
0
PPM

Figure C-4

^{13}C NMR Spectrum of $[(n^5-C_5H_5)Fe(CO)]_2(u\text{-DPPE})$, II



where P—P = $(Ph_2P)_2C_2H_4$

Figure C-5

^1H NMR Spectrum of $[(n^5\text{-}C_5H_5)Fe(CO)]_2(u\text{-}DPPP)$, III

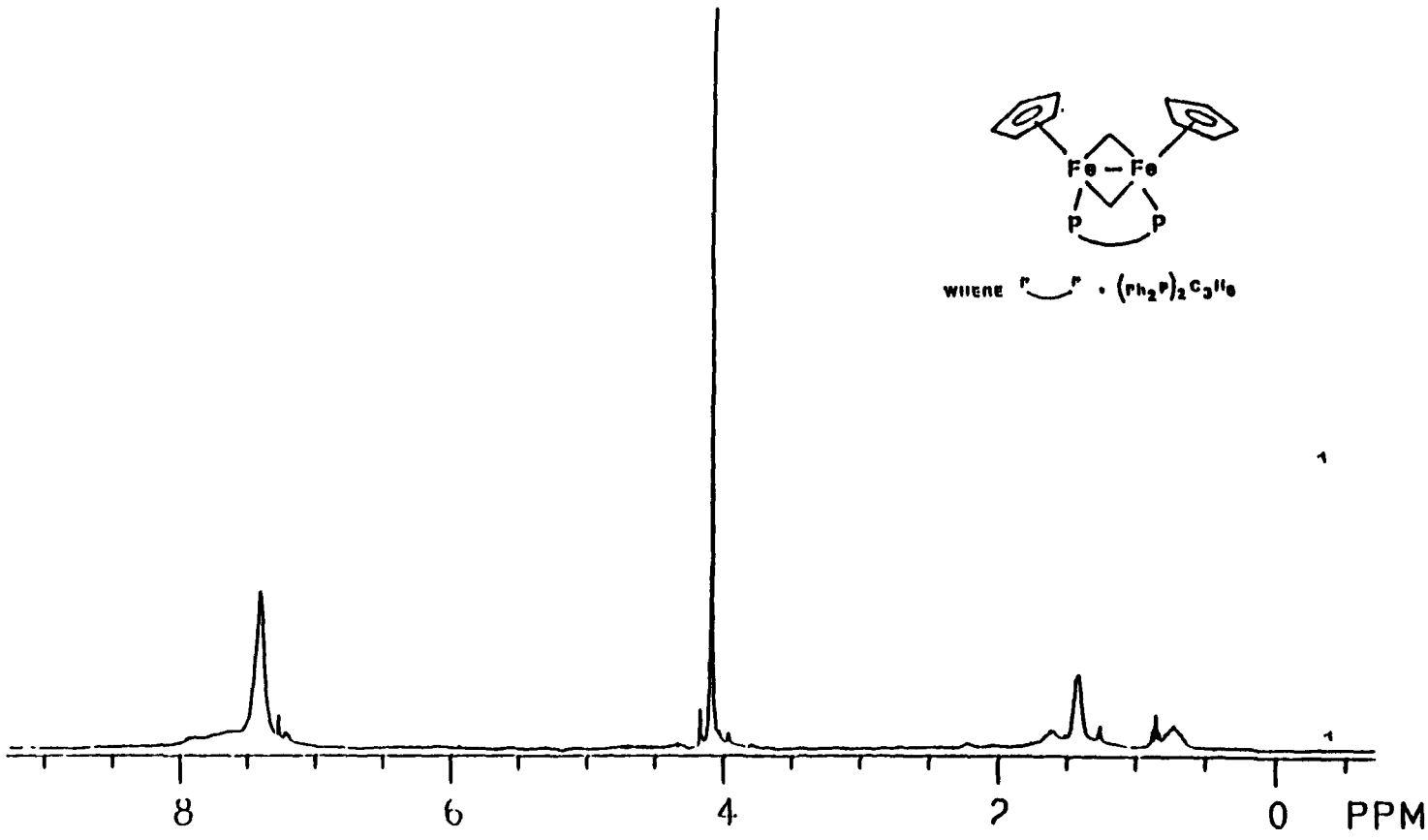

Fe — Fe
P P
WHERE P⌒P = (Ph2P)2C3H6
8
6
4
2
0
PPM

Figure C-6

^1H NMR Spectrum of $(n^5\text{-}C_5H_5)(n^5\text{-}C_5H_4CHO)Fe_2(CO)_2(u\text{-}DPPM)$, IV

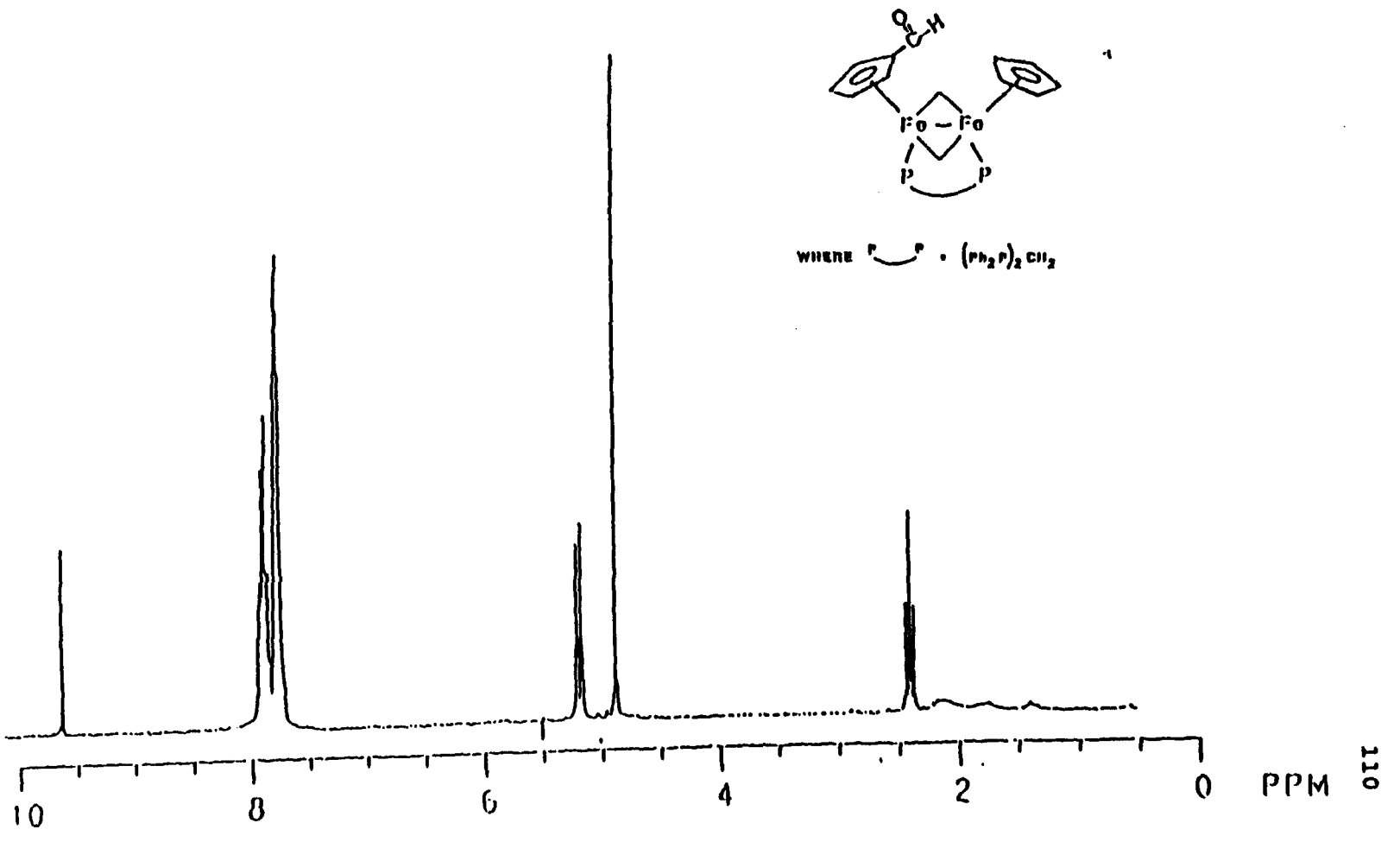
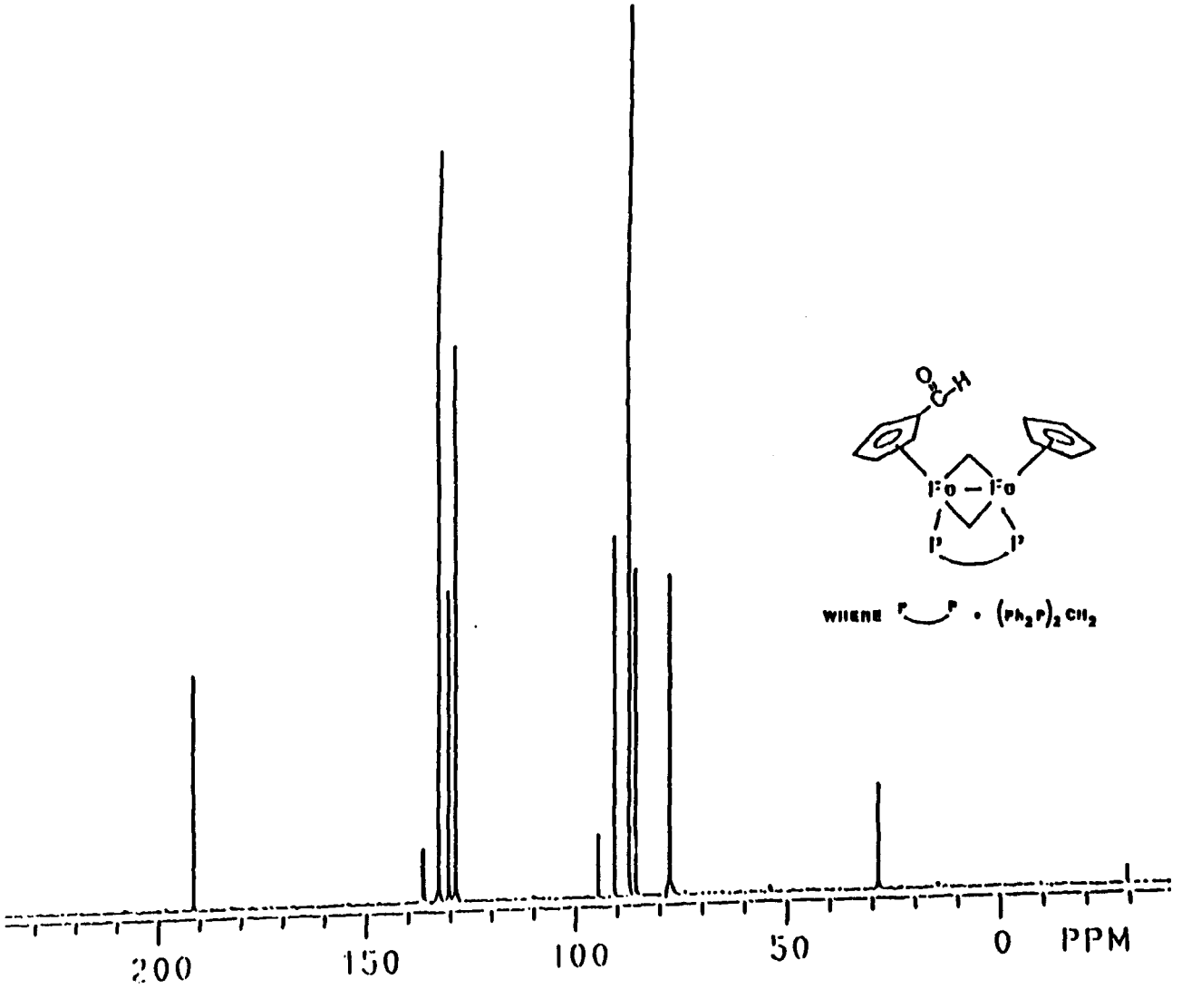

O
C
H
Fe
Fe
P
P
WHERE P⌒P = (Ph2P)2CH2
10
8
6
4
2
0
PPM

Figure C-7

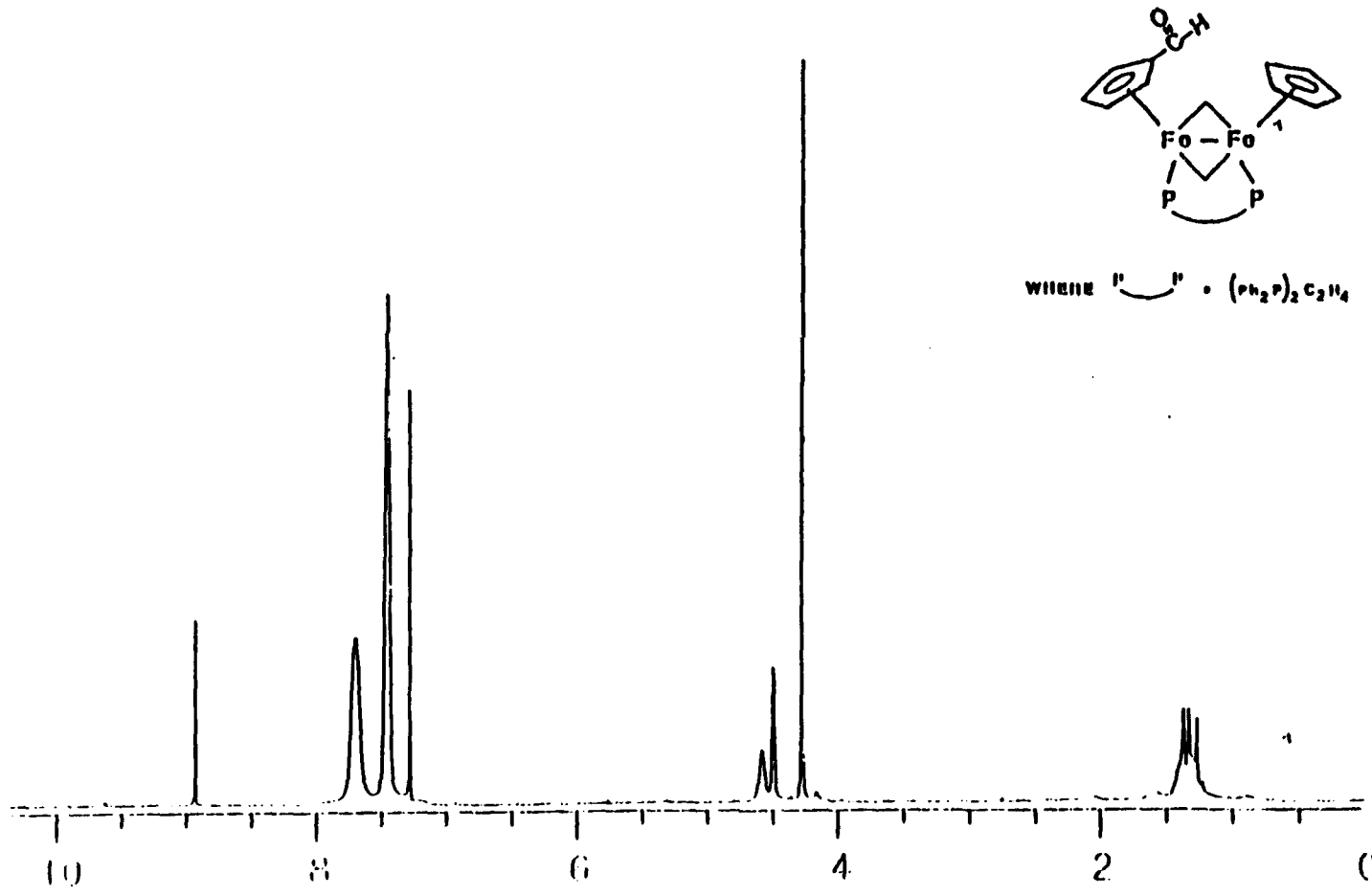
^{13}C NMR Spectrum of $(n^5\text{-}C_5H_5)(n^5\text{-}C_5H_4CHO)Fe_2(CO)_2(u\text{-}DPPM)$, IV



WHERE $\overset{P}{\frown}\overset{P}{}$ = $(Ph_2P)_2CH_2$

Figure C-8

^1H NMR Spectrum of $(n^5\text{-}C_5H_5)(n^5\text{-}C_5H_4CHO)Fe_2(CO)_2(u\text{-}DPPE)$, V



where "⌒" = $(Ph_2P)_2C_2H_4$

Figure C-9

^{13}C NMR Spectrum of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CHO)Fe_2(CO)_2(u\text{-}DPPE)$, V

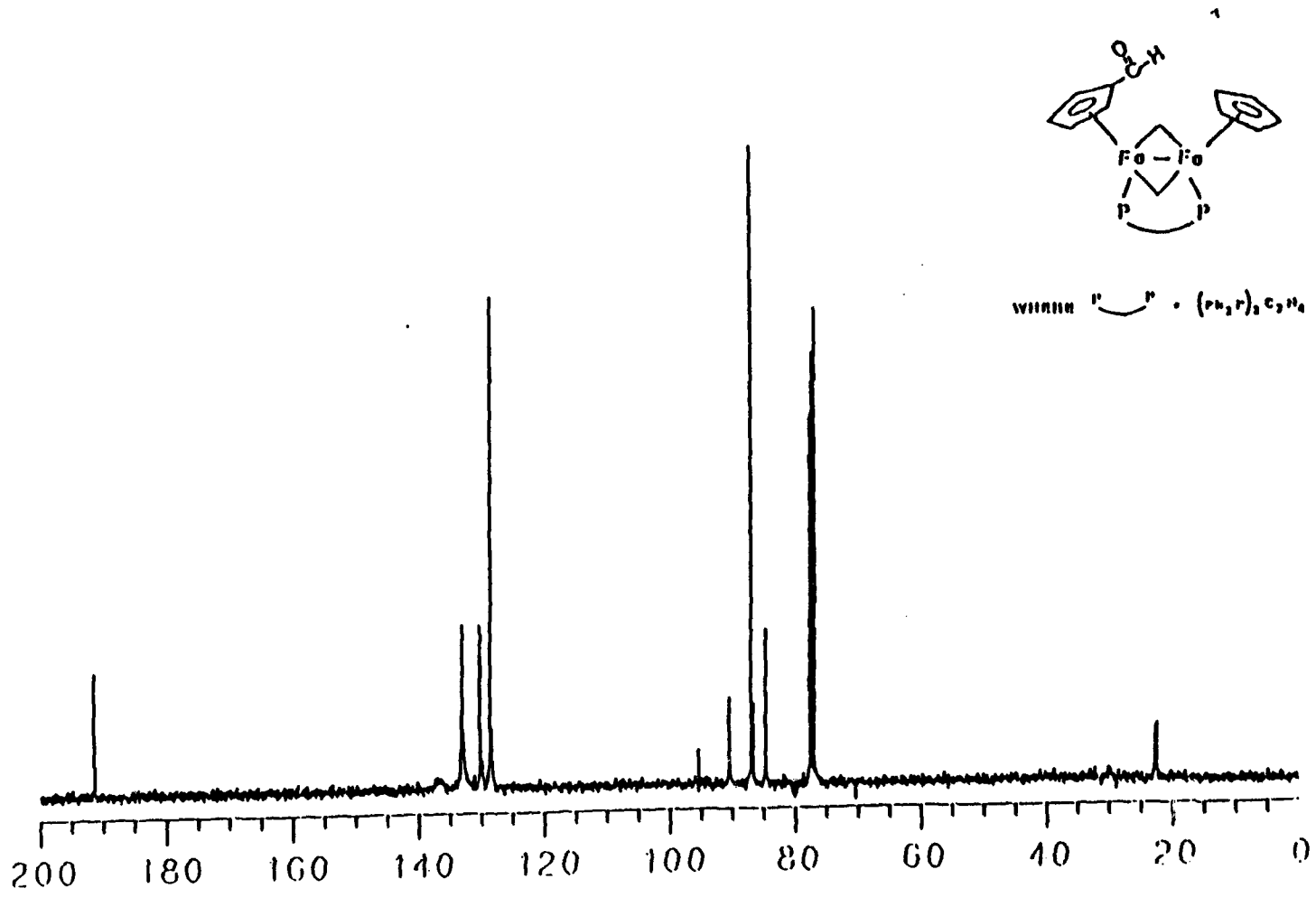

200
180
160
140
120
100
80
60
40
20
0
PPM

Figure C-10

^1H NMR Spectrum of $[(n^5\text{-}C_5H_5)Ru(CO)]_2(u\text{-}DPPM)$, VII

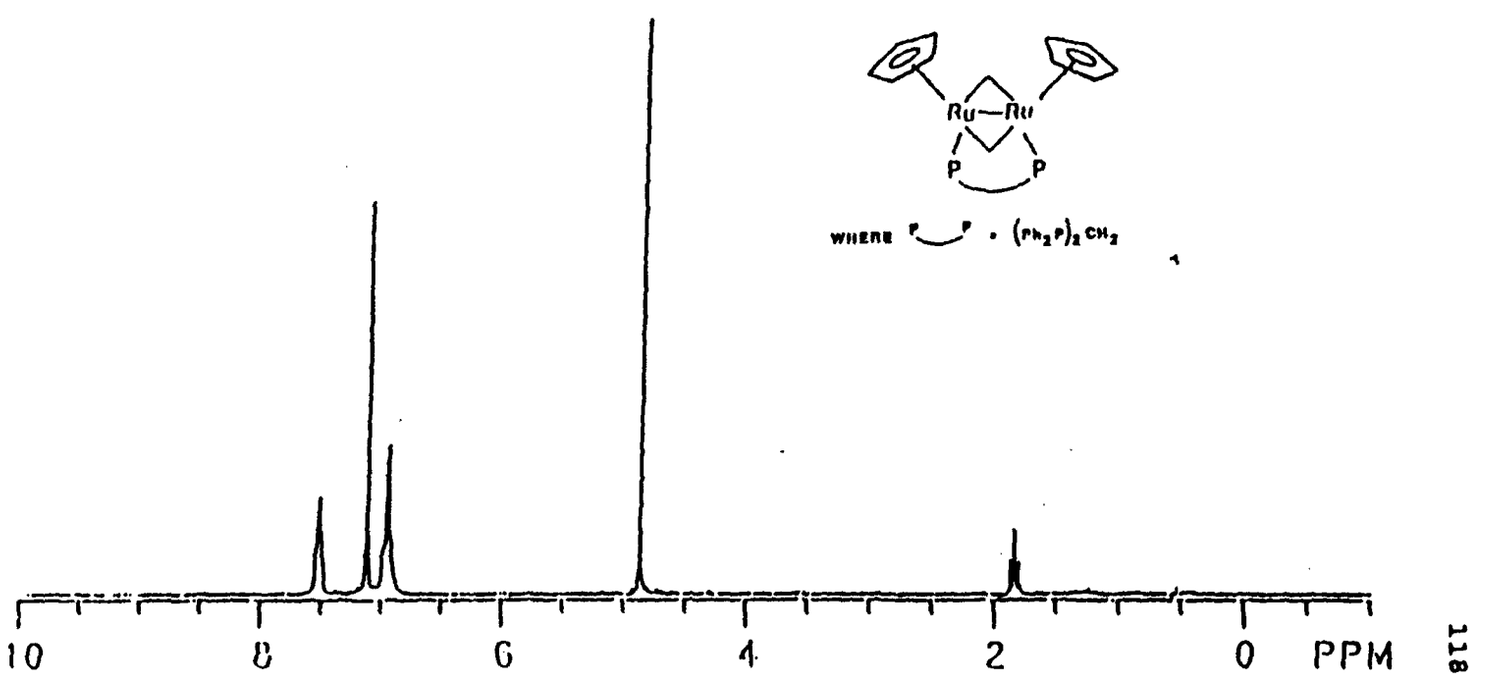
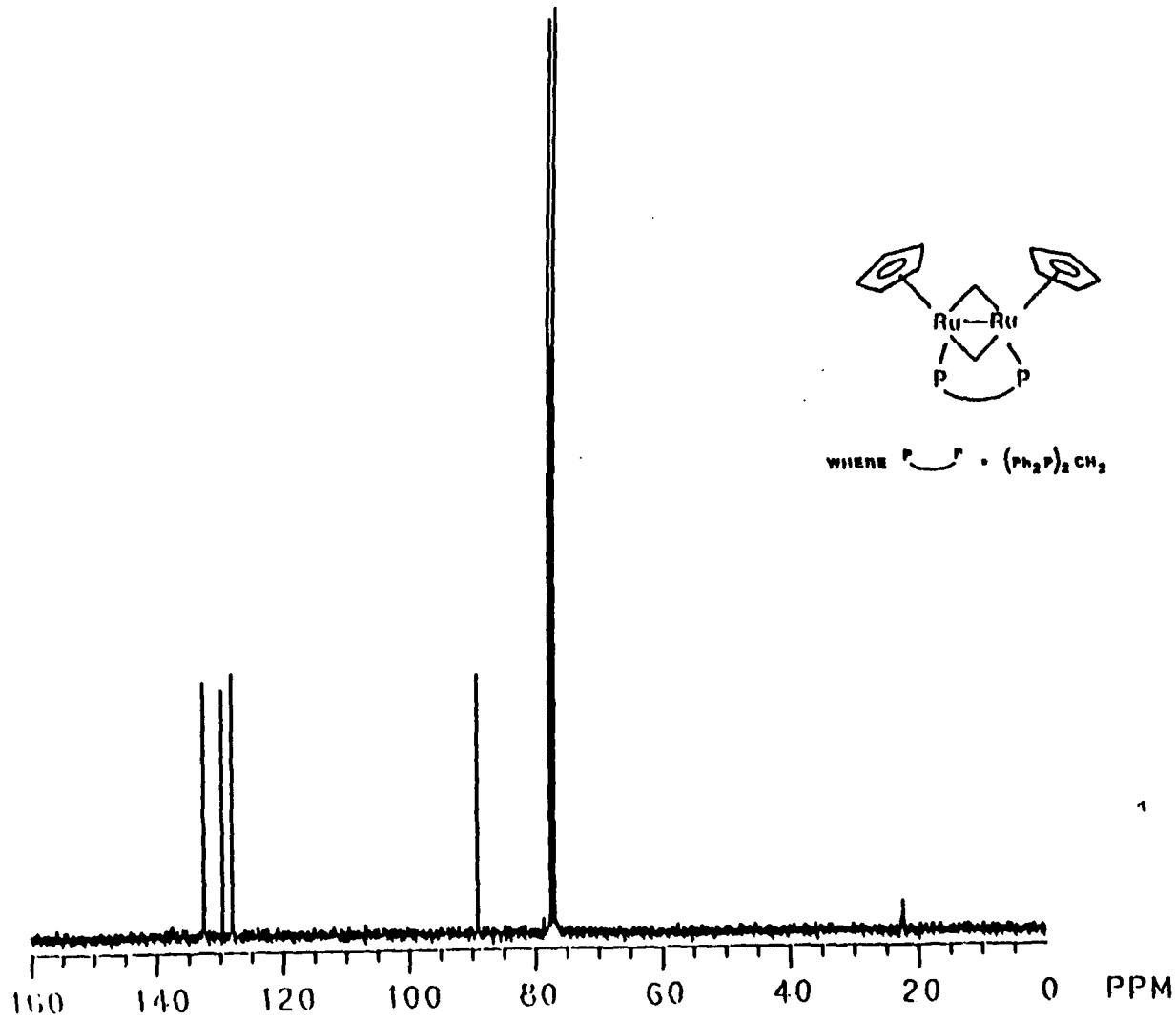

Ru—Ru
P
P
WHERE P⌒P = (Ph2P)2CH2
10
8
6
4
2
0
PPM

Figure C-11

^{13}C NMR Spectrum of $[(\eta^5\text{-}C_5H_5)Ru(CO)]_2(\mu\text{-DPPM})$, VII



WHERE $P\frown P = (Ph_2P)_2CH_2$

Figure C-12

^1H NMR Spectrum of $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CHO)Ru_2(CO)_2(u\text{-}DPPM)$, VIII

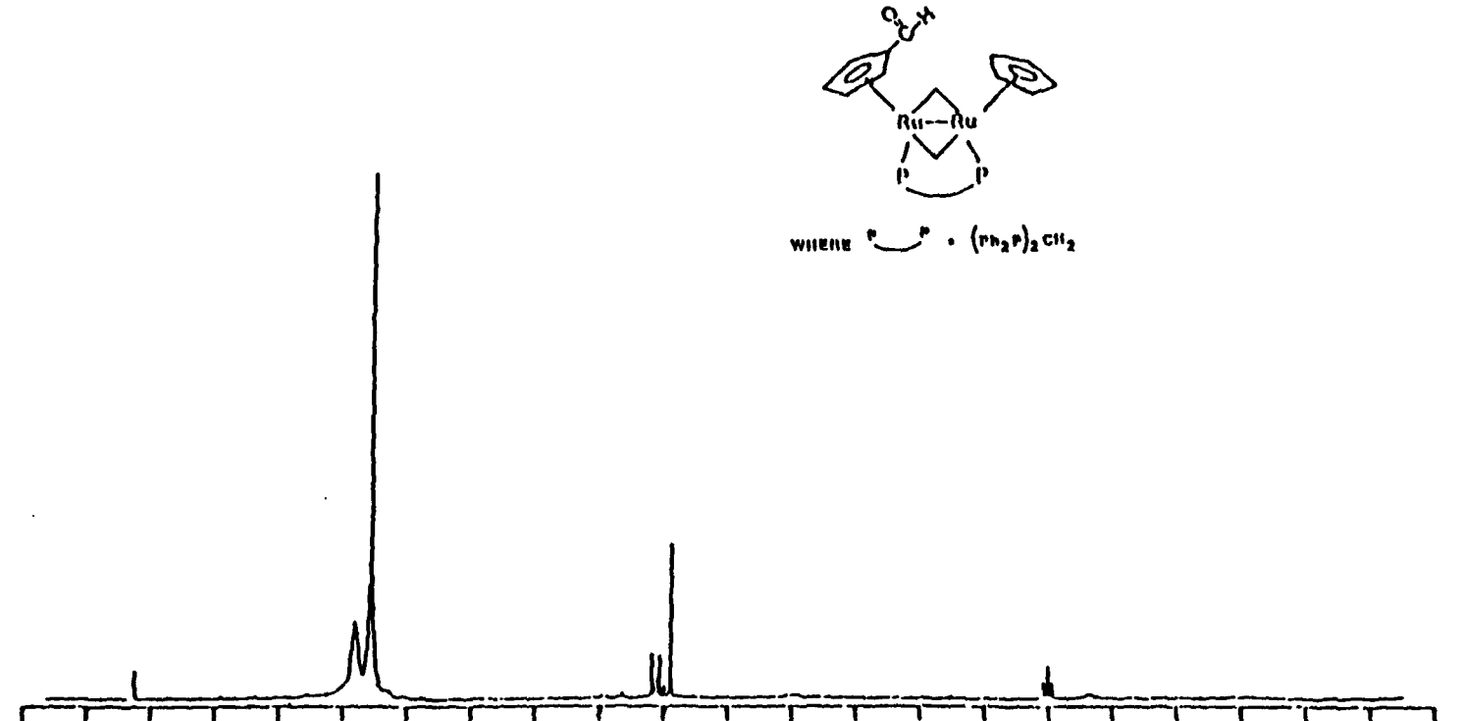

Ru—Ru
P
P
10
8
6
4
2
0
PPM

Figure C-13

^1H NMR Spectrum of $(\eta^5\text{-}C_5H_5)Ru(Cl)DPPM$, IX

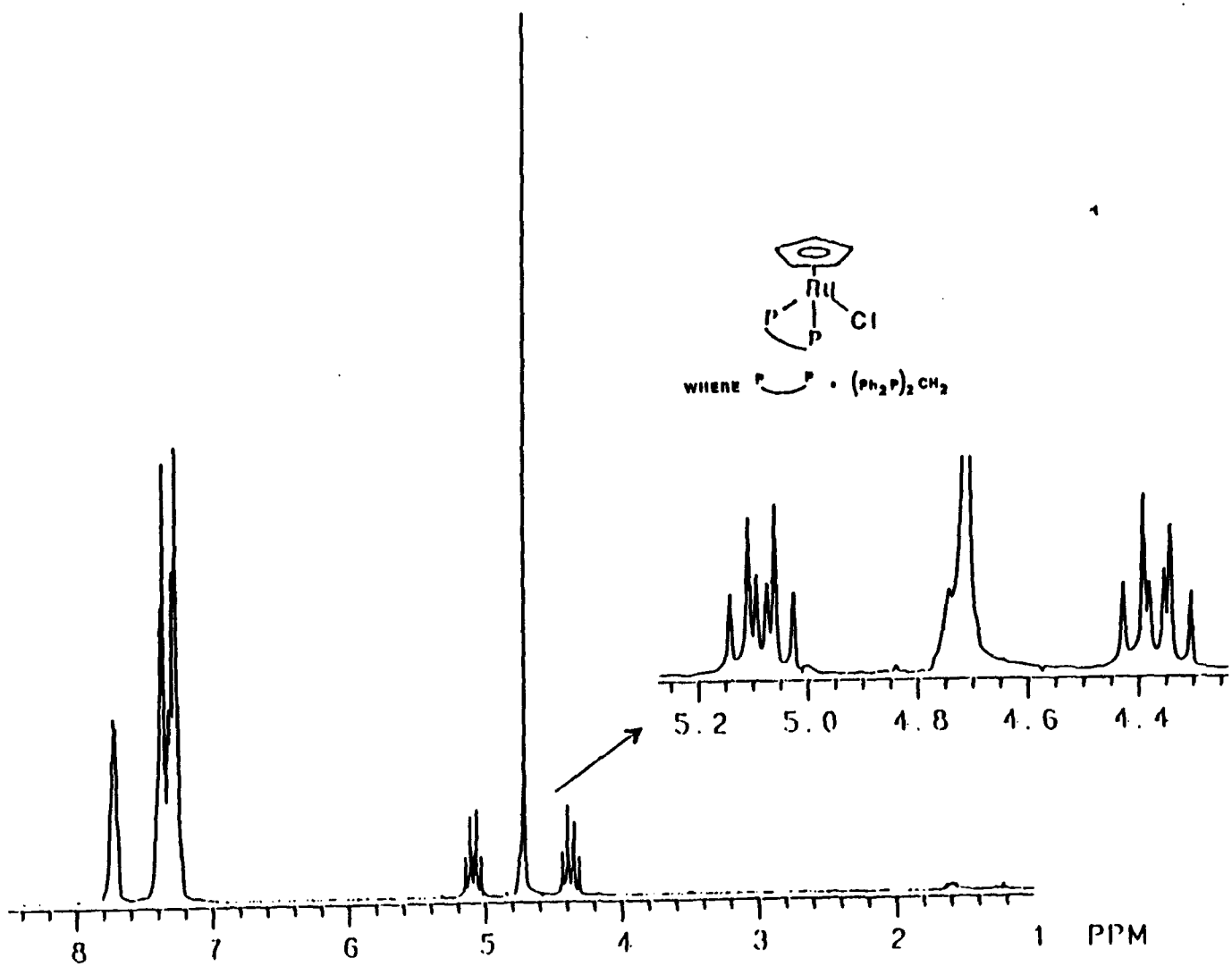
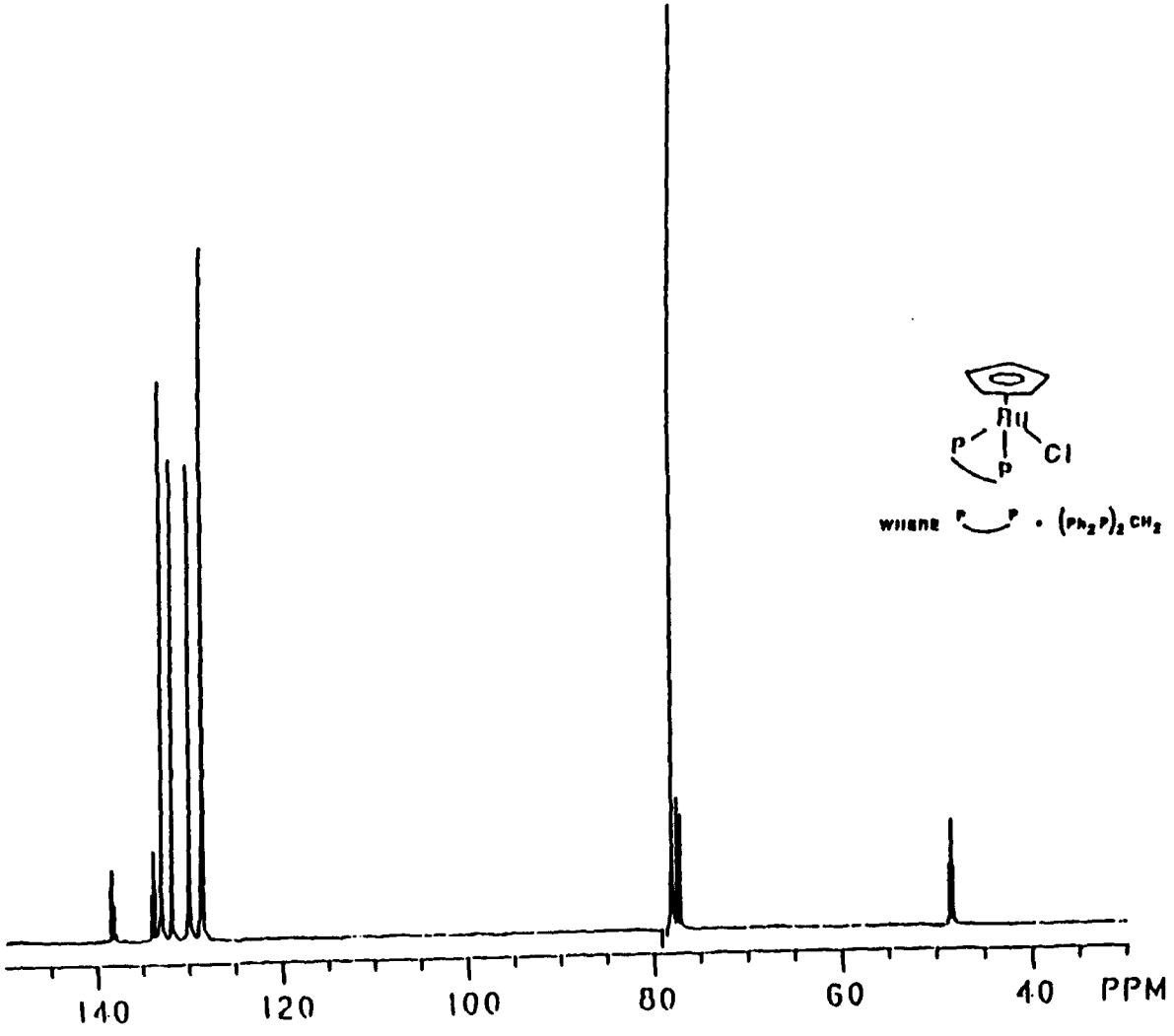

Ru
Cl
P
P
WHERE P⌒P = (PH2P)2CH2
5.2
5.0
4.8
4.6
4.4
8
7
6
5
4
3
2
1
PPM

Figure C-14

^{13}C NMR Spectrum of (n^5-C_5H_5)Ru(Cl)DPPM, IX

with an Expanded Phenyl Region Included


Ru
P
P
Cl
WHERE P⌒P = (Ph2P)2CH2
140
120
100
80
60
40
PPM

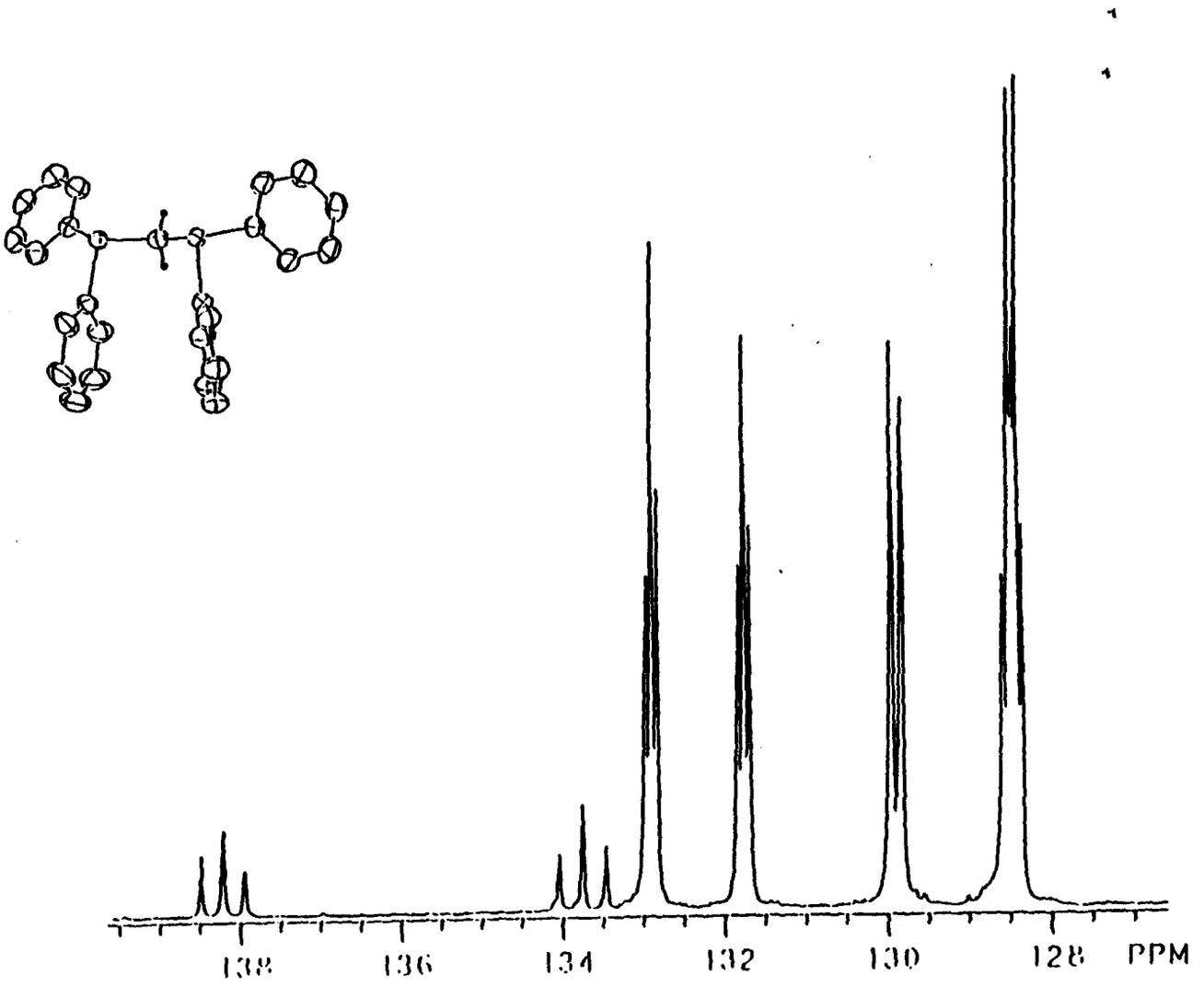

138
136
134
132
130
128
PPM

Figure C-15

^1H NMR Spectrum of $(\eta^5\text{-}C_5H_5)Ru(Cl)DPPE$, **X**

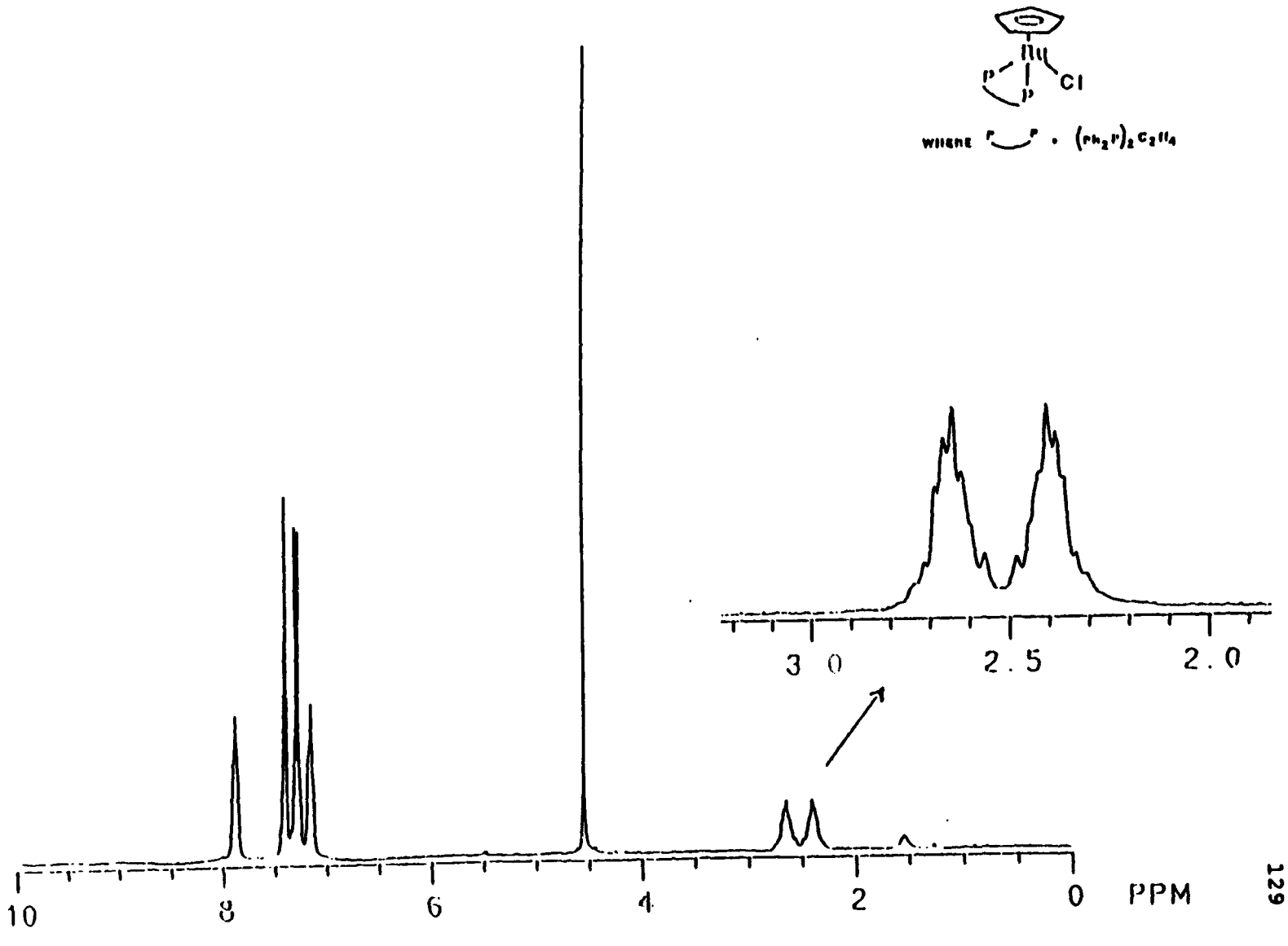
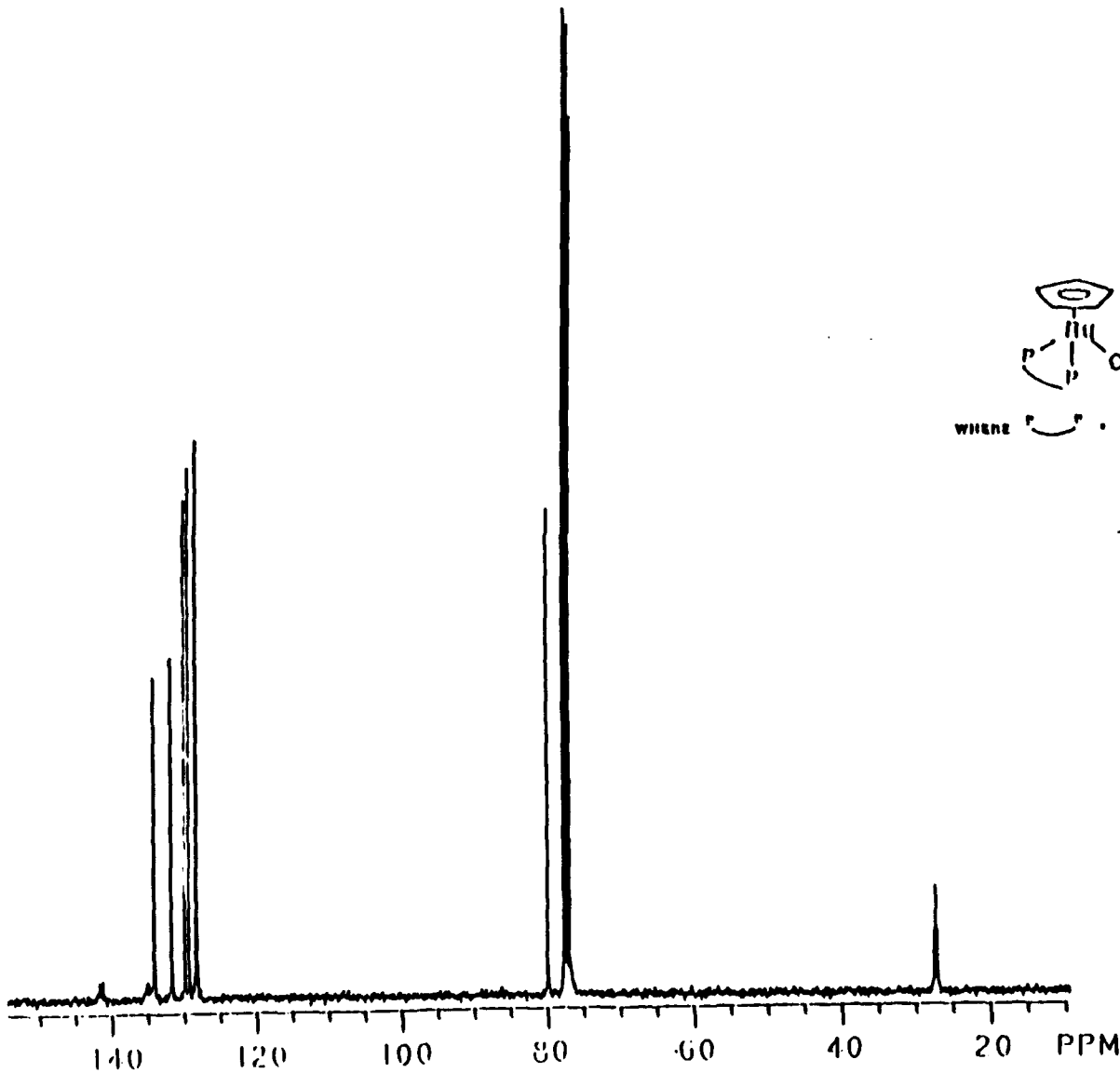

Ru
P
P
Cl
where P⌒P = (Ph2P)2C2H4
3.0
2.5
2.0
10
8
6
4
2
0
PPM

Figure C-16

^{13}C NMR Spectrum of $(n^5\text{-}C_5H_5)Ru(Cl)DPPE$, X


Cl
P
P
P
WHERE P⌒P = (Ph2P)2C2H4
140
120
100
80
60
40
20
PPM

Appendix D:

^{31}P NMR Chemical Shift Data

Table D-1. ^{31}P NMR Data for Compounds I - VII, IX and X.

Compound[a]	Chemical Shift (ppm)[b]
I. FeDPPM	86.63
II. FeDPPE	69.76
III. FeDPPP	59.16
IV. FeDPPM Photo	84.48, 81.47 (J_{p-p} = 92.38 Hz)
V. FeDPPE Photo	68.52, 64.11
VI. FeDPPP Photo	33.32
VII. RuDPPM	64.99
IX. CpRu(Cl)DPPM	13.61
X. CpRu(Cl)DPPE	80.23

[a]Spectra recorded in $CDCl_3$ at ambient temperature.
[b]Chemical shifts are relative to 85% H_3PO_4 in a coaxial tube.